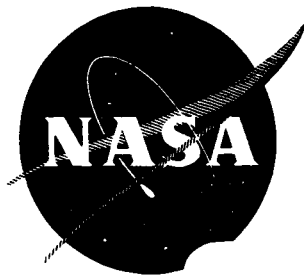


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NASA CR-54045
8413-6014-SU-000



N64-22193
CODE-1 CAT-23.
NASA CR-54045

ION EMITTER STUDIES

by

A. CHO AND H. SHELTON

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Contract NAS 3-2524

OTS PRICE

XEROX

MICROFILM

\$ 8.10 per page
\$ none

TRW SPACE TECHNOLOGY LABORATORIES

THOMPSON RAMO WOOLDRIDGE INC.

FINAL REPORT

ION EMITTER STUDIES

by

A. Cho and H. Shelton

prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

May 11, 1964

CONTRACT NAS 3-2524

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ION EMITTER STUDIES

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ABSTRACT

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The effect of impurities on the cesium ion and neutral emission from hot porous tungsten are presented. These impurities include oxygen, carbon, calcium, silicon, boron, fluorine, and chlorine. The cesium neutral fraction and the critical temperature, when the clean or contaminated porous tungsten is emitting ions, are correlated with the work function and cesium binding energy inferred from the electron emission "S" shaped curve.

Authn

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ION EMITTER STUDIES

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SUMMARY

Clean tungsten produced by operation and ion sputtering in an oxygen-free, hydrocarbon-free vacuum, when emitting less than about 1 nano-ampere per pore, exhibits the cesium neutral, ion and electron emission characteristics of solid tungsten. Oxygenated tungsten (dependent on the degree of oxygenation) has a higher work function, produces a lower neutral fraction and a higher critical temperature. Its neutral fraction is distinguished by its constancy with temperature to hundreds of degrees above the critical temperature. Porous tungsten, lightly carbided, also has a higher work function, and so produces a lower neutral fraction, but also has a lower critical temperature because of the low binding energy of cesium to this surface. Calcium is a bad poison because it lowers the tungsten work function and raises the cesium binding energy. The neutral fraction rises at high ion current density when the density of surface pores is insufficient, or the pore distribution is poor, so that some areas are overfed. Often in this case, the critical temperature is not sharp and the neutral fraction continues to fall at elevated temperatures instead of rising as the Saha-Langmuir equation predicts and as observed at lower ion current densities.

INTRODUCTION

This report covers the work done during the last year under Contract NAS 3-2524. This program is a continuation of two years work under NAS 8-41. This previous work is described in the Summary Report No. 26 prepared by Space Technology Laboratories for Lewis Research Center. Results of this previous program will be incorporated into this report which gathers into logical form the work reported throughout the year in monthly reports. These monthly reports are recommended only for a clearer picture of the chronological order of experiments and a glimpse into the evolution of theories, right and wrong. A concise presentation of the results of the program related to porous tungsten in general and not to a particular sample is contained in the paper that we read before the January 1964 New York meeting of the AIAA. It is included in this report as an appendix, but might well be read by the casual reader of this report for a description of the experimental apparatus and as a synopsis.

GOALS OF THE PROGRAM

1. To study and identify contaminants and their means of transport and to measure their effect upon cesium ion and atom emission and critical temperature.
2. To increase the current density at which measurement can be made and identify the conditions allowing less than 1% neutral fraction at an ion current density of 10 ma/cm^2 .

3. To study improved ionizer materials and methods of preparation which will reduce neutrals from porous tungsten operating at high current densities.
4. To study electron drain currents and to identify the mechanisms involved.

These goals were met. Oxygen, carbon, calcium, fluorine, silicon and boron were studied. Measurements were conducted up to 16 ma/cm^2 and an improved accelerating scheme has been proposed for extending the measurements well beyond this. Small-grain porous tungsten with a high pore count has been shown to be better than coarse-grain, and surface etching has been shown to improve the operation of porous tungsten. Drain currents have been shown to be field enhanced thermionic and field emission electron currents from low work function points covered with cesium compounds.

CONTAMINANTS STUDY

In order for a contaminant to alter the neutral or ion emission, it must reside on the surface in significant quantities. Many materials will be evaporated off at a greater rate than they arrive because of their low binding energy on tungsten and the high temperature of the tungsten. A graph is presented in figure 1 that relates the arrival rates (equivalent gas pressure in torr), evaporation energy, and the tungsten temperature in order to maintain a coverage of approximately 0.1 monolayer. We use the approximation that 10^{-6} torr represents a particle current density of $4 \times 10^{14}/\text{cm}^2/\text{sec}$.
| actually, $\Gamma = 4.13 \times 10^{14} \times \sqrt{\frac{29}{M} \times \frac{300}{T} \frac{P}{10^{-6}}}$ | and that 0.1 monolayer is

$4 \times 10^{13}/\text{cm}^2$. Therefore the arrival rate is $4 \times 10^{14} \frac{P}{10^{-6}}$. This is equated against the evaporation rate σ/τ where the surface coverage σ is 4×10^{13} and the evaporation lifetime τ is $10^{-13} \times 10^{\frac{5040 E}{T}}$ where E is the activation energy in volts (1 volts equals 23 K cal/mole) so $\frac{4 \times 10^{14} P}{10^{-6}} = 4 \times 10^{13} \times 10^{+13} 10^{-\frac{5040 E}{T}}$. $\therefore P = 10^{+6} 10^{-\frac{5040 E}{T}}$. This relation is plotted in figure 1. If the tungsten operating temperature is 1500°K and the arrival rate is equivalent to 10^{-7} torr (0.1 monolayer/sec) we can see from the graph that only materials with a binding energy of greater than about 90 K cal/mole will accumulate as much as 0.1 monolayers, and be of concern to us. If a material has a very large work-function variation and the binding energy is only slightly below 90 or suspicion exists that it has higher than the measured binding energy to certain sites on the tungsten, or in the presence of some other material such as oxygen, we must still consider it.

In table 1 is a list of approximate evaporation binding energies⁽¹⁾ for dilute films on tungsten.

TABLE I

<u>Molecules</u>	<u>E (K cal/mole)</u>	<u>Molecules</u>	<u>E (K cal/mole)</u>
A	2	N ₂	85
B	140	N	153
Ba [100]	87	O ₂	194
CS	64	O	147

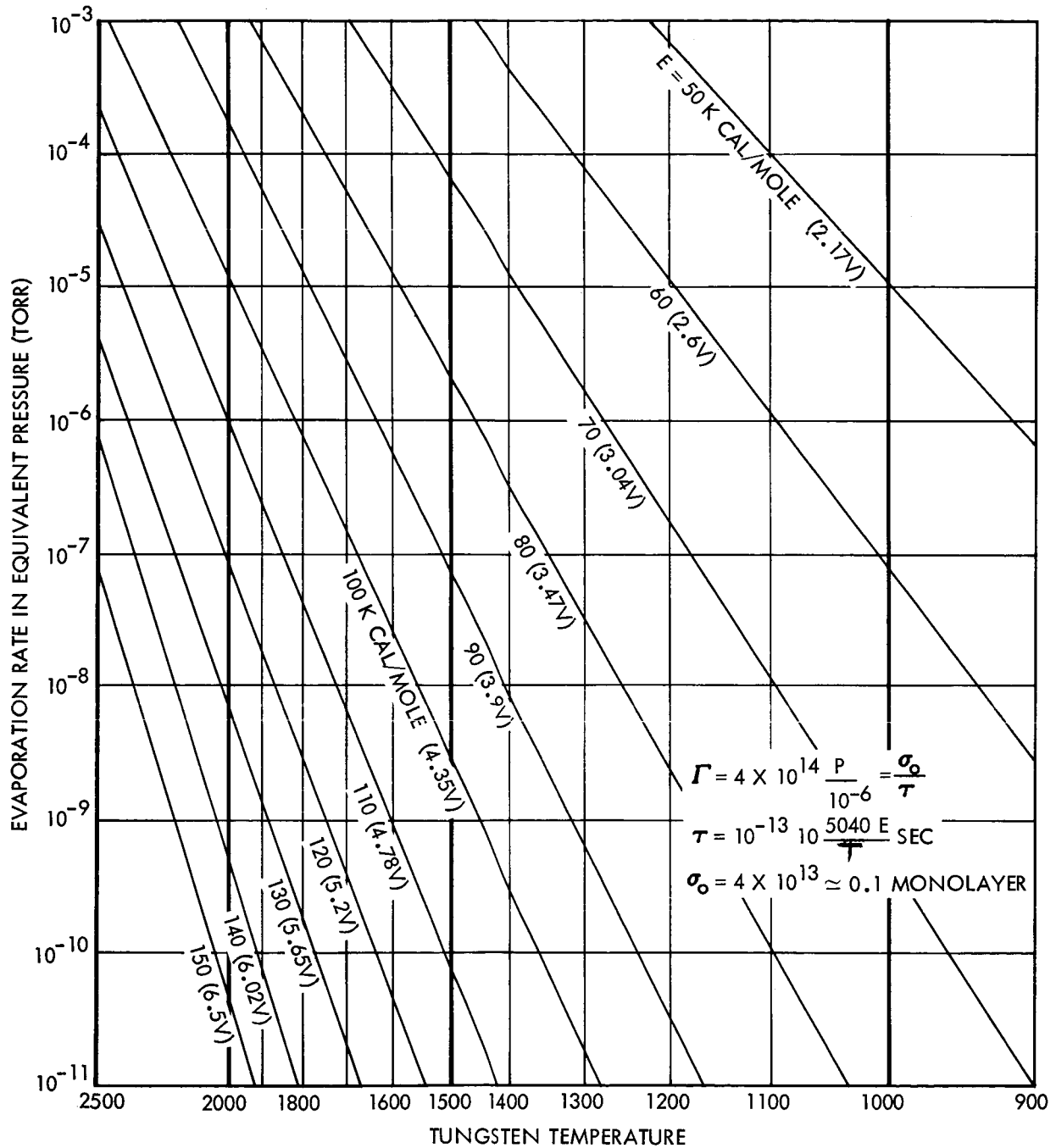


Figure 1. Graph relating arrival (or evaporation) rate to maintain 0.1 monolayer for different binding energies and temperatures.

<u>Molecules</u>	<u>E (K cal/mole)</u>	<u>Molecules</u>	<u>E (K cal/mole)</u>
CO	77 ⁽²⁾ 100	Rb	60
CO ₂	122	Xe	9
H ₂	46		

From this list, we see we can disregard the inert gases, H₂, CO, and N₂ and the alkali metals. Of certain concern would be O₂, O, B and C (not on list). N would come off as N₂, CO₂ would probably come off as CO. Barium is of concern because of its high value which is undoubtedly higher for other crystallographic directions(e.g., [110]) and if oxygen is present. Because of the acceptably low value of the binding energy of CO⁽²⁾, carbon will be of no concern if an excess of oxygen is present. Also, oxygen will be of no concern if an excess of carbon is present.

Of the materials mentioned so far, the material that would be of most concern, if it were a poison, would be boron because of its high binding energy and the lack of other known boron compounds with a smaller energy. However, it is a small atom, diffuses interstitially, and as confirmed by experiments in this program was never expected to alter the work-function of tungsten.

There is a large list of materials that would be very difficult to get rid of and that also are known to reduce the work-function of tungsten. These include thorium and zirconium. It would be very bad if these materials were supplied in the porous tungsten as solid solution or inclusions of oxides of these metals. It is only hoped that these materials are eliminated in the manu-

facturing process by chemistry of the powder metallurgy or in the higher temperatures involved in the sintering.

Other materials if exposure continues will essentially never evaporate, but will cover the surface and expose the new surface. If the exposure stops soon enough, the surface concentration will dilute itself by diffusion into the tungsten. These include Rhodium, Molybdenum, Rhenium, Titanium, Vanadium, Platinum, Iridium, and Tantalum.

There are innumerable other elements and infinite combinations that might be considered. However, we will confine our discussion to materials that have some likelihood of arriving at the surface. The arrival to the surface can be from the interior of the porous tungsten from contaminants in the tungsten or contaminants supplied with the cesium. It can arrive on the front surface by evaporating or being sputtered from adjacent parts or by coming as a gas from the vacuum, or outgassing of adjacent parts.

The materials studied have a high likelihood of being found on the surface of porous tungsten. Oxygen is present in porous tungsten after exposure to air as an adsorbed monolayer, bulk tungsten oxide, adsorbed water, cesium oxide or hydroxide (if previously exposed to cesium) or as oxides of other refractory metal impurities in the porous tungsten. Oxygen can accompany the cesium if the boiler temperature is high enough. It can come from the vacuum system as O_2 , H_2O , or CO_2 . Carbon might be included in solid solution in the porous tungsten, might be brought

with the cesium as some volatile cesium compound ($\text{Cs}_2\text{C}_2?$) or a hydrocarbon. Carbon might come from the vacuum system as a hydrocarbon fraction of the pump oils. Calcium can be expected to be included as an impurity in the porous tungsten from some manufacturers. Silicon can be expected as an impurity in the porous tungsten and might be deposited from sputtering or baking the glass of the vacuum system. Boron might be from the glass or a difficult to avoid impurity in the tungsten. Fluorine could possibly come from the glass, or in our case, from teflon gaskets in our vacuum system.

Oxygen

Confusion exists as to the method oxygen in small coverage leaves tungsten. Ehrlich suggests it would come off as atomic oxygen with a binding energy of 147 K cal/mole. Becker, Becker and Brandes⁽³⁾ suggest molecular oxygen comes off with a binding energy of 105 K cal/mole. We tend to believe the high value applies to the last remnants of oxygen, while the lower value applies when in equilibrium with an oxygen pressure between 10^{-9} and 10^{-6} torr. The following analysis is based on the higher value. It is supported by the molecular adsorption energy at 194 K cal/mole determined by calorimetric methods.⁽⁴⁾

The evaporation rate of 0.1 monolayer of atomic oxygen ($E = 149$ K cal/mole) from tungsten at 1500°K would be 10^5 atoms/ $\text{cm}^2/\text{sec.}$, a rate that would take many years to significantly alter the coverage. To remove the oxygen, then, one must look for other

transport processes. Of concern in any such process is the rapidity of surface migration of such an oxygen film. In Ehrlich's fine article on surface adsorption are tabulated data on surface migration of oxygen which allow us to estimate the surface diffusion at 1500°K to be about $10^{-4} \text{ cm}^2/\text{sec.}$ (5). If a pore were 1 micron in diameter and 1 millimeter long with a difference of 0.1 monolayer between its two ends, we would expect $D \pi d \frac{d \sigma}{d x} = 10^{-4} \times 3.14 \times 10^{-4} \times 4 \times 10^{13} \times 10^{\sim 7} = 10^7$ particles/pore/sec. With a pore count of $10^6/\text{cm}^2$, 10^{13} particles/ cm^2 would arrive at a surface per sec. - 0.1 monolayer in 4 seconds, rather than the many years it would take to evaporate off.

With the negligible evaporation rate, we inquire as to how the oxygen might be removed. Under many circumstances carbon diffusing from solid solution to the surface and there combining with oxygen to form volatile CO is the dominant oxygen removal mechanism. Becker (3) gives the diffusion constant of carbon in tungsten as $D = 1.6 \times 10^{-6} \exp \left(-\frac{11000}{T} \right) = 3 \times 10^{-13} \text{ cm}^2/\text{sec.}$ at 1500°K . If one atom percent of carbon is at an effective depth of one micron, the arrival rate at the surface will be $3 \times 10^{-13} \times 6 \times 10^{20} \times 10^4 = 2 \times 10^{12}$ carbon atoms/ $\text{cm}^2/\text{sec.}$ This rate could remove 0.1 monolayers in 20 seconds. This carbon concentration gradient would exist after a time of approximately $\frac{L^2}{D} = \frac{10^{-8}}{3 \times 10^{-13}} = 3 \times 10^4$ seconds. At times less than this, the carbon concentration gradient would be larger and hence could rid the surface of oxygen even more rapidly. It seems likely that there remains enough carbon in the tungsten even after days of heating in oxygen to handle many

monolayers of oxygen over the entire interior surface of the porous tungsten. This is because of the large diffusive time constant of grains of tungsten 5 microns in diameter $T = \frac{d^2}{\pi^2 D} = \frac{25 \times 10^{-8}}{10 \times 3 \times 10^{-13}} = 10^5 \text{ sec.}$ However, the small grain size does favor the carbon removal, especially if the oxygen exposure is maintained for many days, or if the temperature is higher.

This discussion has involved the removal of a residual surface coverage of oxygen without continuous replenishment. We note that the carbon diffusion rate to the surface can't compete with an oxygen arrival rate greater than 10^{-8} torr. If the mobility of oxygen is as great as previously calculated and the oxygen arrives on the outside surface, and yet carbon diffuses to the surface of all the pores throughout the porous tungsten, a larger rate of oxygen arrival could be handled by carbon diffusion. As more and more data on the adsorption of oxygen on tungsten accumulates, the evidence mounts that there are many different binding states. The suspicion exists that the last traces of oxygen might be bound at sites (lattice steps of certain crystal planes, etc.) so tightly that they are immobile. If this is the case we cannot depend on mechanisms distant from the surface to remove the oxygen.

In the absence of carbon, oxygen might be removed by evaporation of some molecular form of tungsten oxide. It is difficult to assess this possibility at low oxygen coverages. The evaporation energy is equal to the binding energy of each of the constituents minus the combination energy that is released when the

molecule is formed. For WO_3 this is $202 + 147 + 147 + 147 - 550 \approx 90$. This being less than 147 is why WO_3 preferentially desorbs instead of oxygen. This particularly occurs at higher coverage because the rate goes as the cube of the oxygen coverage. In an analogous manner, evaporation of a cesium-oxygen molecule might remove oxygen. The binding energy of a Cs_nO molecule is $147 + 64n - E_f$ where E_f is the energy of formation of the molecule from atomic components. Therefore, there is a possibility of oxygen coming off more readily by this mode than by evaporation of atomic oxygen if $E_f > 64n$. This criterion is that the compound should be stable compared to adsorption energy of cesium. This does not seem to be the case, as might be surmised by the fact that these compounds are known to decompose before they evaporate (low formation energy of the gaseous molecule) while cesium adsorbs quite strongly to tungsten.

Sputtering could remove the oxygen if all else fails. It would be particularly effective if oxygen from the interior pore surfaces wouldn't continuously repopulate the surface. At least the sputtering would compete with the repopulation rate, and if the rate of sputtering were high enough would maintain the surface clean during sputtering. The time it would remain clean after sputtering would depend on the repopulation rate (which, of course, would be higher the higher the tungsten temperature). Our experience with sputtering qualitatively supports this view.

There is much evidence that the adsorption of oxygen and its consequent effect on the work-function of tungsten is not a

simple, easily understood phenomenon - especially at ion emitting temperatures. One does not know how much of the data are affected by carbon. Generally the work-function is seen to range from near 6 volts to that of clean tungsten. It seems clear that the 6 volt figure is found at low temperatures with any oxygen pressure, and at higher temperature ($>1500^{\circ}\text{K}$) only with large oxygen pressure. Any realistic oxygen pressure will raise the work-function a few tenths of a volt to temperatures beyond 2000°K . At 1600°K any measurable oxygen pressure will cause a work-function of over 5 volts. An oxygen pressure of over 10^{-5} torr increases the work-function to over 5.5V. This is to suggest that the surface is neither oxygenated nor clean. It can be forced to be overly oxygenated if operated in a continuous supply of oxygen, or it can have any degree of the remnant coverage. (6,7,8)

Through this work-function increase, cesium neutrals from tungsten emitting ions are reduced by the presence of oxygen. The presence of oxygen also raises the critical temperature. These points are illustrated in figure 2. Most of the characteristics of oxygenated tungsten can be seen here: About a hundred degree increase in critical temperature and a low neutral fraction quite insensitive to increased temperature. However, some interpretations of these curves are necessary. Note that when 5×10^{-7} torr of oxygen is introduced little effect is noted, while after the O_2 is off after sustained heavy exposure, the surface remains oxygenated. Previous to exposure to oxygen the source operated for

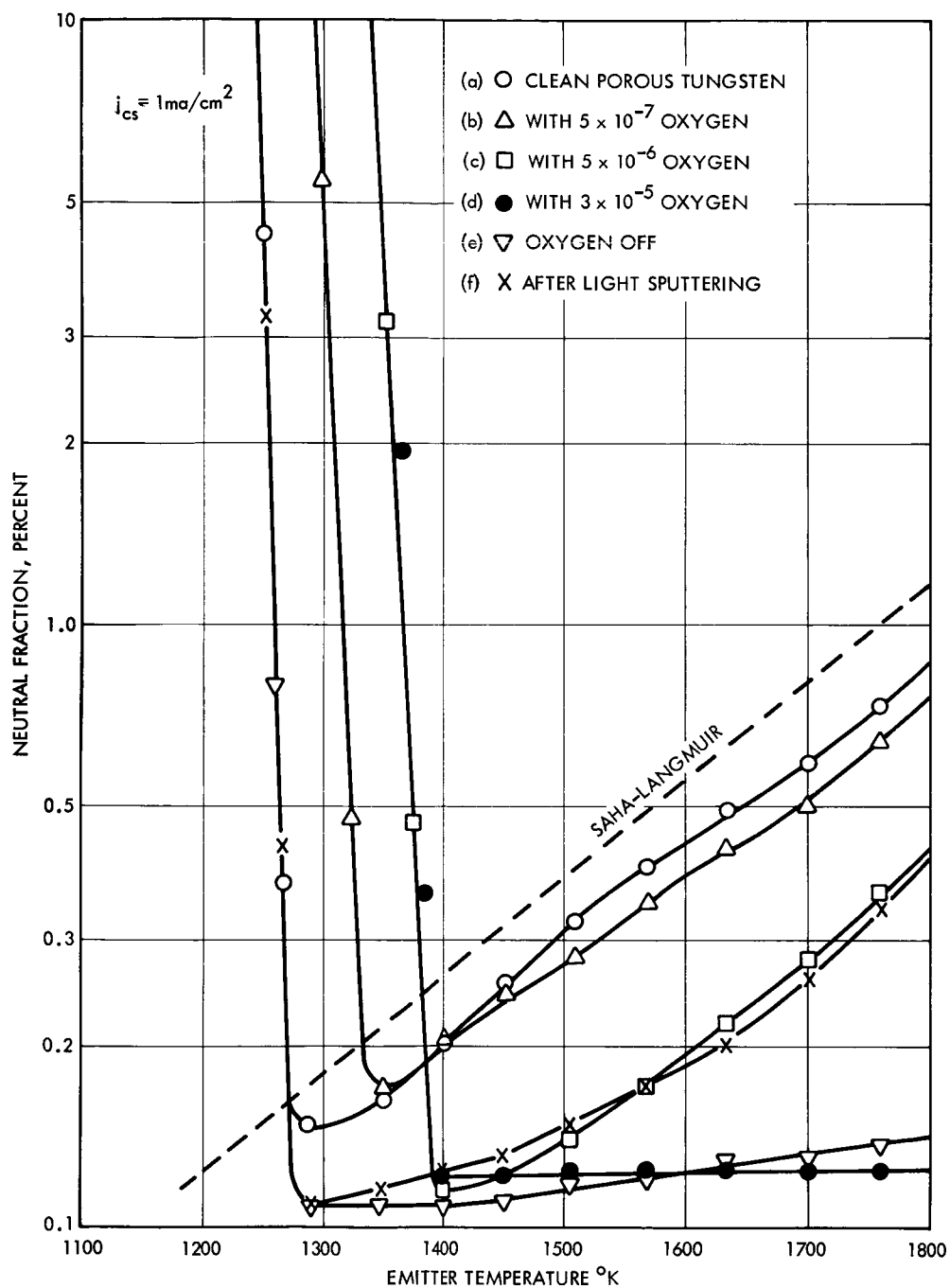


Figure 2. Cesium neutral fraction versus temperature for a porous tungsten ionizer with different stages of oxidation.

long periods under the clean conditions. Concentrations of carbon near the surface could have increased. Therefore when 5×10^{-7} torr of oxygen was first introduced, either carbon converted the oxygen to CO, or the oxygen migrated over the interior pore surface. In any event, there is evidenced little oxygen adsorption at the high temperatures. Data for curve (b) were taken over the span of minutes from high temperature downward. Possibly by the time the lower temperatures were reached, oxygen accumulated through the reduced diffusion of carbon causing an increase in critical temperature. Curve (c) at 5×10^{-6} oxygen is showing a characteristic of oxygenated tungsten at low temperature but evidencing more rapid than normal oxygen removal at the high temperature. Curve (d) is typical of an oxygenated surface, the high oxygen pressure was necessary, probably to combat the competing effect of carbon. This is exemplified by the characteristics of an oxygenated surface even at high temperatures after the oxygen is turned off. At this time the surface concentration gradient of carbon has been reduced by prolonged removal by oxygen conversion to CO and the interior pore surfaces are saturated with oxygen so if need be, oxygen can be supplied to the front surface by migration. Why the critical temperature has returned to its original value is unknown. The difficulty of getting rid of this oxygen is illustrated in curve (f) showing the partial removal of oxygen by light sputtering. More time and sputtering eventually produces the clean tungsten characteristics. Seen on this

curve is the value of neutrals predicted by the Saha-Langmuir equation, (% fraction) $\approx 200 \exp - e(4.7-3.9)/kT$. It can be seen that the value of the neutrals from clean tungsten and their dependence on temperature is quite close to that predicted by theory. This is because the data were taken at 1 ma/cm^2 where the pore distribution of this porous tungsten did not yet alter the results from solid tungsten.

The effect of oxygen on the electron emitting characteristics of the same porous tungsten is seen in figure 3. Predicted electron current densities at different work functions calculated from the Richardson equation with $A = 120$ are shown as straight lines. Here again the effects of first introducing only a small oxygen pressure is seen (curve c); the effects are only at low temperature where increased low temperature electron emission results. Operation in an oxygen pressure results (curves d and e) when lowering the temperature in a rise of electron current at higher temperatures than previously and then a suppression of the low temperature electron emission. This latter effect might be expected if the oxygen arrival rate exceeded the cesium arrival rate, but this is not the case. The answer must involve the creation of a thicker than monolayer coverage on the tungsten at the low temperatures - most likely an oxide layer. The excess cesium evaporates from the top of the layer more rapidly and is not bound as tightly. At higher oxygen arrival rates, the coating is thicker and the work-function is greater. This explanation can help explain the observed hysteresis effect. Note in curve (a) that when a source is first put in service after exposure to air, the electron emission is characteristic of heavy oxygenation. This poisoning of electron emission at low temperatures by

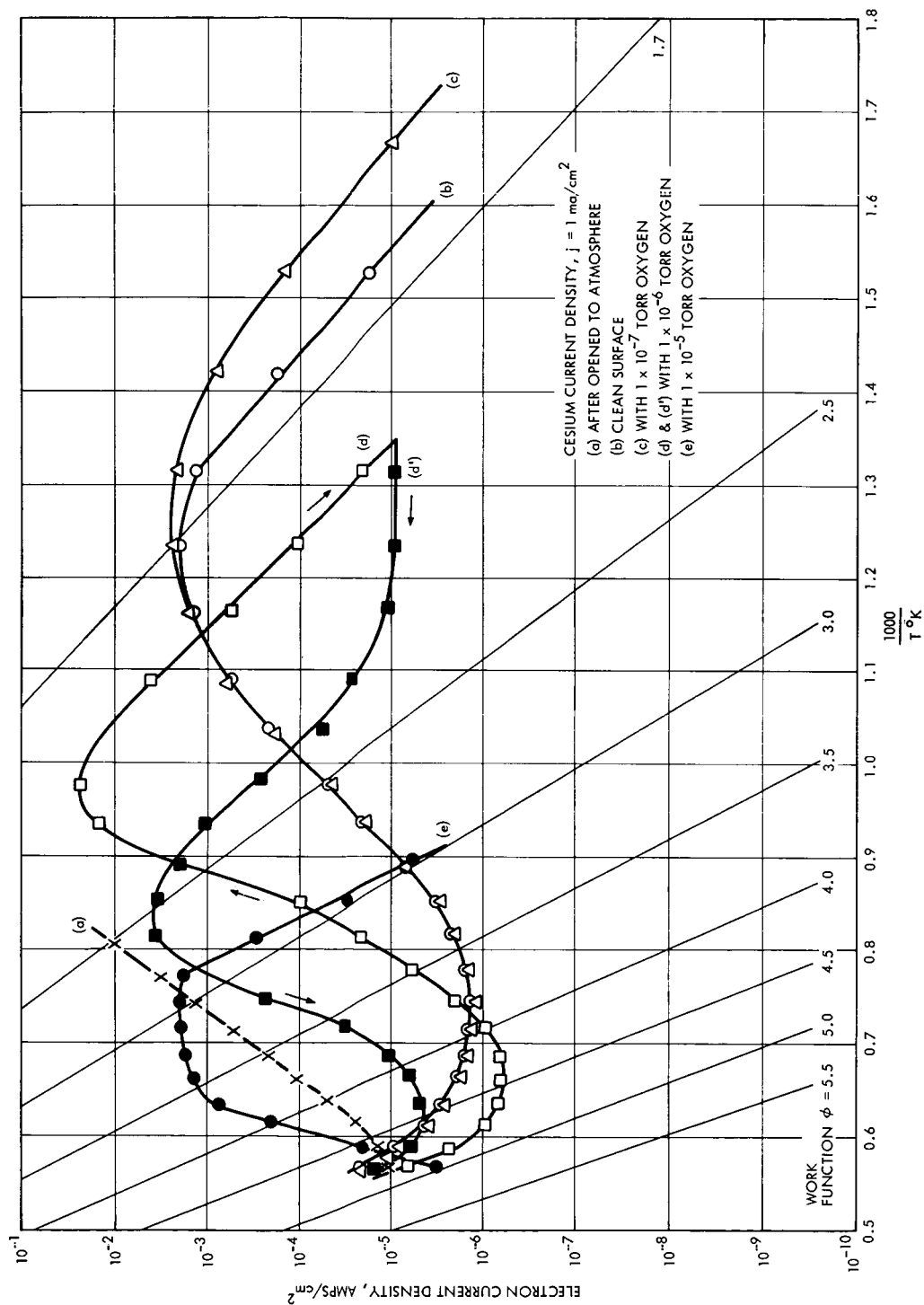


Figure 3. Electron emission "S" shaped curves for porous tungsten ionizer with different oxygen pressures.

introducing oxygen, has been used by us as a last resort at times for reducing drain currents.

The very beneficial effect of oxygen at high current density in reducing both neutrals and the temperature at which a source may operate is shown in figure 4. Here the poor pore distribution removes the distinct critical temperature so low neutrals require quite a high temperature. Oxygenated tungsten has a much more distinct critical temperature and although higher than for clean, one can operate closer to the critical temperature and therefore actually cooler.

In the ion engine working at high current densities where the neutral fraction might otherwise be excessive and both lower the mass efficiency and life by charge-exchange sputtering, it might be beneficial to operate oxygenated by continuing to supply a small amount of oxygen. The most serious obstacle to this scheme is the possible removal of tungsten from the source by volatilization of tungsten oxide. Data⁽³⁾ on the evaporation rate of WO_3 under continuous exposure to oxygen at greater than 10^{-7} torr appear to agree that at $1500^\circ K$ approximately 1% of the oxygen is effective in taking away an atom of tungsten. The theory of Becker⁽³⁾ predicts 0.3% at 10^{-9} torr of oxygen. In one year of operation, this would amount to only 30 layers deep - an unmeasurable amount. It seems reasonable that a continuous exposure of 1×10^{-7} torr of oxygen could be tolerated. We feel that this certainly would force the tungsten to be sufficiently oxygenated that the major neutral reduction would be gained.

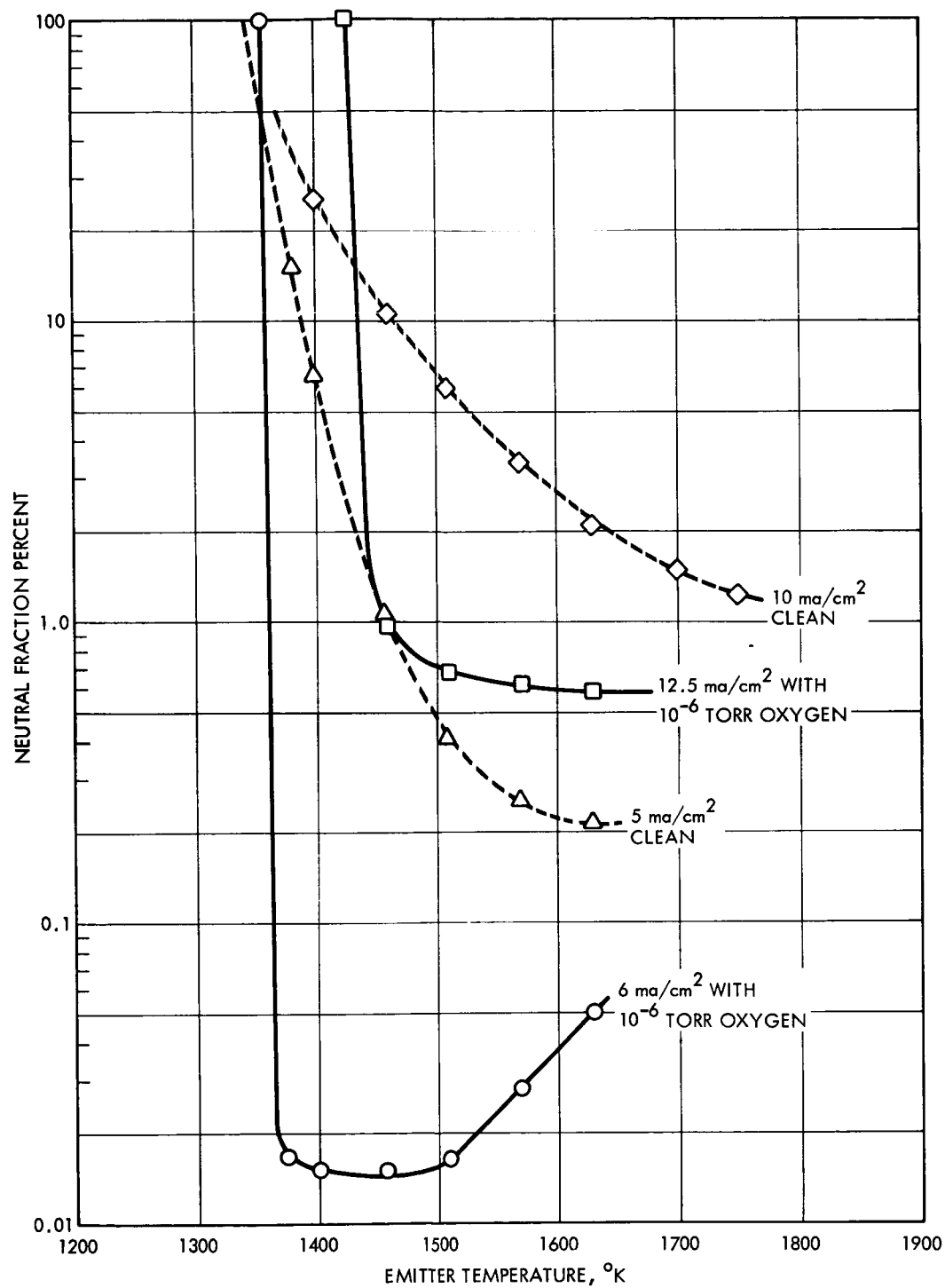


Figure 4. Cesium neutral fraction versus porous tungsten temperature showing the beneficial effects of oxygen at high current densities.

Delivering the oxygen to the source in such a manner that cesium would not getter the oxygen first, could be a problem. A very fine hole facing the emitter a few inches away and out of the ion beam would be exposed to a reduced neutral density and have a very much higher local oxygen density. As long as the oxygen current density at the small orifice is greater than the cesium arrival rate, the oxygen will not be seriously getterred.

A further effect of oxygen in ion engine technology is its ability to transport ordinarily refractory metals. Tungsten itself can increase its permeability by tungsten transport in the pores by volatilization of oxides. The sintering rate might be enhanced. Worse still, the tungsten might be transported to the surface, plug the pores and impair the high ion current density operation of the emitter⁽⁹⁾. Metals from the feed tube, such as molybdenum, rhenium, etc. can find their way into the porous tungsten by this mechanism.

Carbon

Carbon in tungsten has a very profound influence even on solid tungsten filaments that one uses in ion gauges and other devices used in ultra-high vacuum work, even though these filaments have been rigorously outgassed by extended heating at very high temperatures. Its presence was first detected by a mass spectrometer that observed CO evolved when these tungsten filaments were heated in oxygen. In passing one cannot help but wonder how long

it could have gone undetected if it did not have a volatile oxide. One wonders then if something like boron or silicon might not have an equally profound effect and yet not be detectable. In dilute quantity, carbon does not seem to affect the work-function by itself, but only through its affect on oxygen. This role of carbon has been discussed in the last section. However, when carbon is present on the surface in greater concentrations than can be dissolved into solid solution, the resultant carbide affects the work-function, the binding energy of cesium, and the thermal emissivity. There are four recognized solid states involving combinations of carbon and tungsten. These are: 1) Solid tungsten with up to about 1 atom percent carbon dissolved into it 2) W_2C , a black crystalline material easily identified by X-rays. 3) WC - the hard tool material again easily identified by X-rays. 4) Carbon, most likely amorphous graphite as ordinarily encountered. If a thin layer of carbon is deposited on tungsten and then heated sufficiently hot in vacuum, immediately a thin layer of WC would form next to the carbon and then W_2C between it and the tungsten. The tungsten in contact with the W_2C would have the saturated solid solution concentration of carbon. This concentration is rapidly diluted as one progresses further into the tungsten, and further diffusion of carbon into the tungsten proceeds very slowly because of the small diffusion constant of carbon in the well ordered tight tungsten crystal. The carbon layer will be depleted as rapidly as the carbon can diffuse through the two carbide layers, where it combines with tungsten to form W_2C . The relative thickness of the two carbides is probably governed by the ratio of the diffusion

neutrals at higher temperatures. Clean tungsten is identifiable by its known work-function and its extreme sensitivity to small amounts of oxygen.

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1. Teem, et al, "Ionizer Development and Surface Physics Studies" EOS report 1660/1-IR-1 Pg. 16.
2. Levi - Private Communication. See also JAP 33 Pg. 2336 - July 1962.
3. Hussman, O.K. "A Comparison of the Contact Ionization of Cesium on Tungsten with that of Molybdenum, Tantalum, and Rhenium Surfaces" - 63019 AIAA Conference March 1963.

constants in the two carbides. As soon as the carbon layer is gone, the WC layer depletes itself by the continuing diffusion of carbon through the W_2C layer where it finds some tungsten and makes some more W_2C . When the WC is gone the W_2C becomes thinner at a very much smaller rate by the slow diffusion of carbon into the tungsten. When (and if) the tungsten uniformly reaches its saturation carbon content, the resultant W_2C - its thickness dependent on the original amount of carbon - is stable for all time. If a fixed amount of carbon, small compared to the tungsten, is allowed to come to equilibrium this is the only stable situation.

If the tungsten is used up before the WC layer vanishes, then these two carbide layers will stably exist. If more carbon is now added, the WC layer will grow and the W_2C layer will shrink. When the W_2C layer disappears then carbon can remain on the WC.

It is the stable W_2C layer that can exist with an excess of tungsten that we have felt has been the surface on which we have made repeated emissivity and cesium neutral measurements. Usually we put only a thin film on the porous tungsten and then later strip it off by burning in oxygen or allowing it to deplete itself of carbon diffusing into the tungsten at high temperature. This has restricted us from making routine X-ray identification of this surface. At one time we did identify the surface carbided and stabilized in our usual manner and showing a high emissivity by X-rays; the only carbide present was W_2C .

In porous tungsten, if carbon is deposited on the walls of the pores to some depth below the surface for a long enough period, the entire grains near the surface might be converted into WC. This might explain other workers' problems with carburizing, and also why a one inch source used elsewhere in this laboratory for long periods in indiscriminately trapped oil diffusion pump system upon X-ray analysis was proven to be 100% WC - the X-rays could find no W_2C nor W!

Carburization has been accomplished in many different manners: sooting from a flame, rubbing an acetone solution of carbon on the surface, cracking C_2H_2 , cracking C_2F_2 , and sputtering carbon onto the source by immersing graphite in the ion beam. After stabilization at high temperature the results are always the same: increased thermal emissivity, increased work-function and decreased binding energy for cesium. A typical cracking procedure used before one study was to crack C_2H_2 at a pressure of 5×10^{-6} torr for one hour at $1850^\circ K$. Much shorter times have been used when we were not interested in studying the surface for a long period of time including high temperatures. To get rid of the carbon in the surface formed in the above manner would probably require about an hour at 5×10^{-5} torr of pure oxygen. Evidence of returning back to the non-carbided surface starts appearing with a lowering of emissivity and after cycling of high temperature and more oxygen, the characteristics of oxygenated tungsten appear. If the oxygen is turned off when oxygenated characteristics first appear, heating to high temperatures will usually reestablish the carbide characteristics, requiring more oxygen for complete removal.

Once during carburization a poisoned condition results. This poisoning later disappeared. At a much later time when carbon was sputtered on at ion operating temperatures, the initial effect was to increase neutrals. However, when this surface was heated to above 1800°K for a short time the familiar "carbide" surface was in evidence. Later sputtering of carbon onto this surface did not increase the now very low value of neutrals. This suggests that there might be some threshold temperature for the formation of the desirous surface and that once it starts to form, more can form easily at reduced temperatures.

Very good confirmation of these findings and conclusions are provided by the work of J. B. Baker and G. B. Gaines⁽¹⁰⁾. They clearly find less electron emission from a W_2C layer than for clean tungsten and ten times more emission from WC. Their progression of states from free carbon to WC to W_2C and finally to clean W is clearly demonstrated.

Figure 5 illustrates the difference between the desirous carbide layer and clean tungsten. Here the electron emission is shown versus emitter temperature with a constant cesium feed rate. The straight line portion of the carbide curve at high temperature indicates a work-function increase from 4.7 volts for clean tungsten to about 4.9 volts. This will result in less neutrals under ion emission. The nearly two decade lower "valley" indicates that a smaller cesium coverage exists at any temperature in the ion

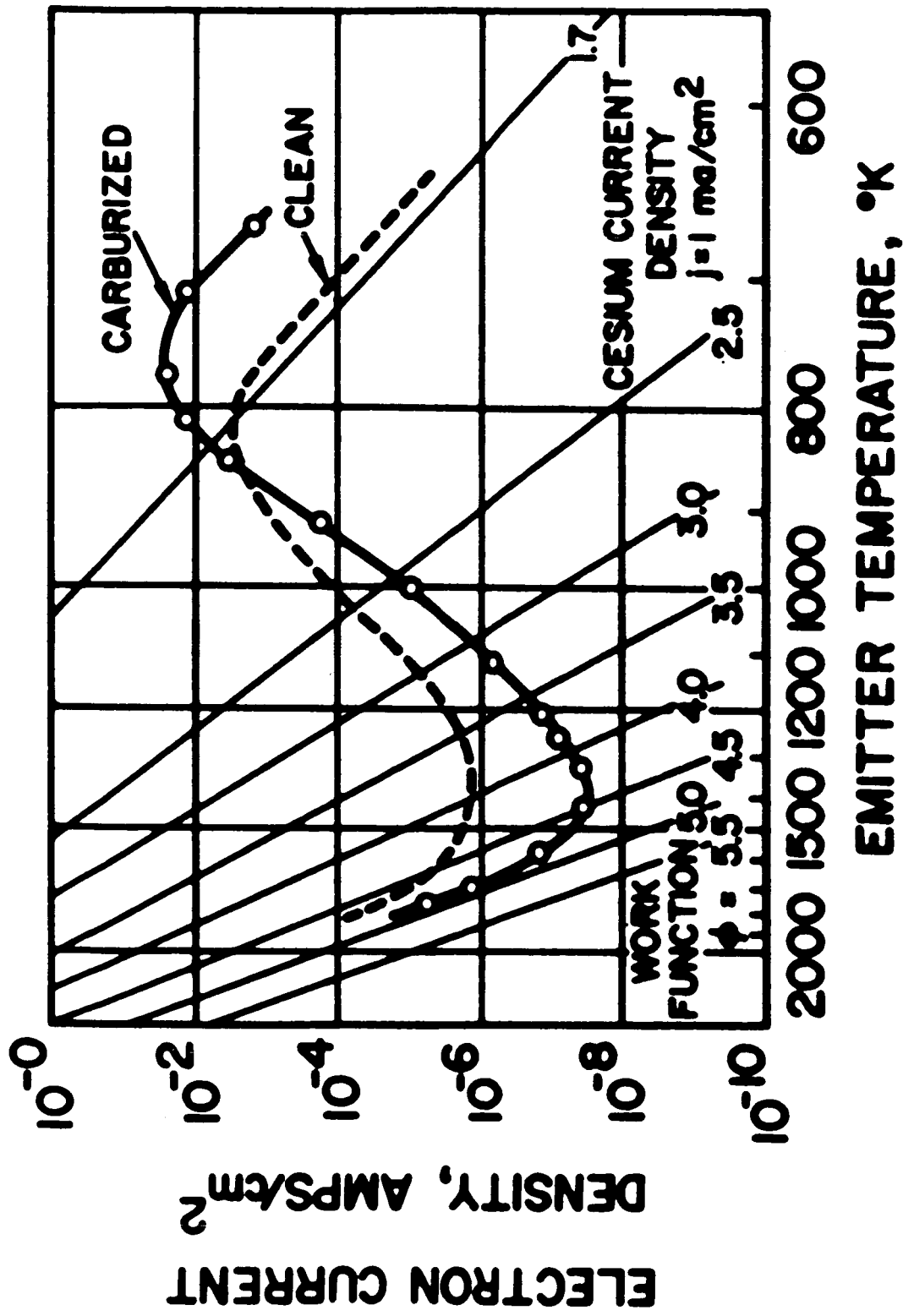


FIGURE 5. ELECTRON EMISSION "S" SHAPED CURVE FOR CARBURIZED POROUS TUNGSTEN IONIZER

emitting range and that the cesium binding energy is less. This will decrease the critical temperature. An observation has been that the temperature at which the work-function is about 3.7 volts for electron emission will be the critical temperature under ion emission. This is equivalent to the observation that just below the critical temperature the ion current is about 10% of that at high temperatures. The Saha-Langmuir equation predicts a ratio of 10:1 between neutrals and ions for 3.7 volts and 1500°K . This criterion predicts 1200°K as the critical temperature for the carbide and 1300°K for the clean tungsten. This is, indeed, the case. A further characteristic of the "S" shaped curve for the carbide is the high electron emission at low temperatures. This carbide holds cesium more tightly at low temperature and less tightly at high temperature than does clean tungsten. Carbon is known to act in a similar manner for barium cathodes. Carbon is used to inhibit electron emission at higher temperatures by allowing the barium to evaporate. At low temperatures electron emission is enhanced by the carbide. (11)

The ion emission characteristics are shown in figure 6. The critical temperature is at 1200°K as predicted. The neutrals are lower than for clean tungsten and the neutrals have nearly the value and temperature dependence predicted by the Saha-Langmuir equation. $\% \text{ fraction} = 100 \left[1 + \frac{1}{2} \exp \frac{e(\phi - 3.9)}{kT} \right]^{-1}$. The steady decline of neutrals as temperature is decreased to within a few degrees of critical temperature is a characteristic of this surface.

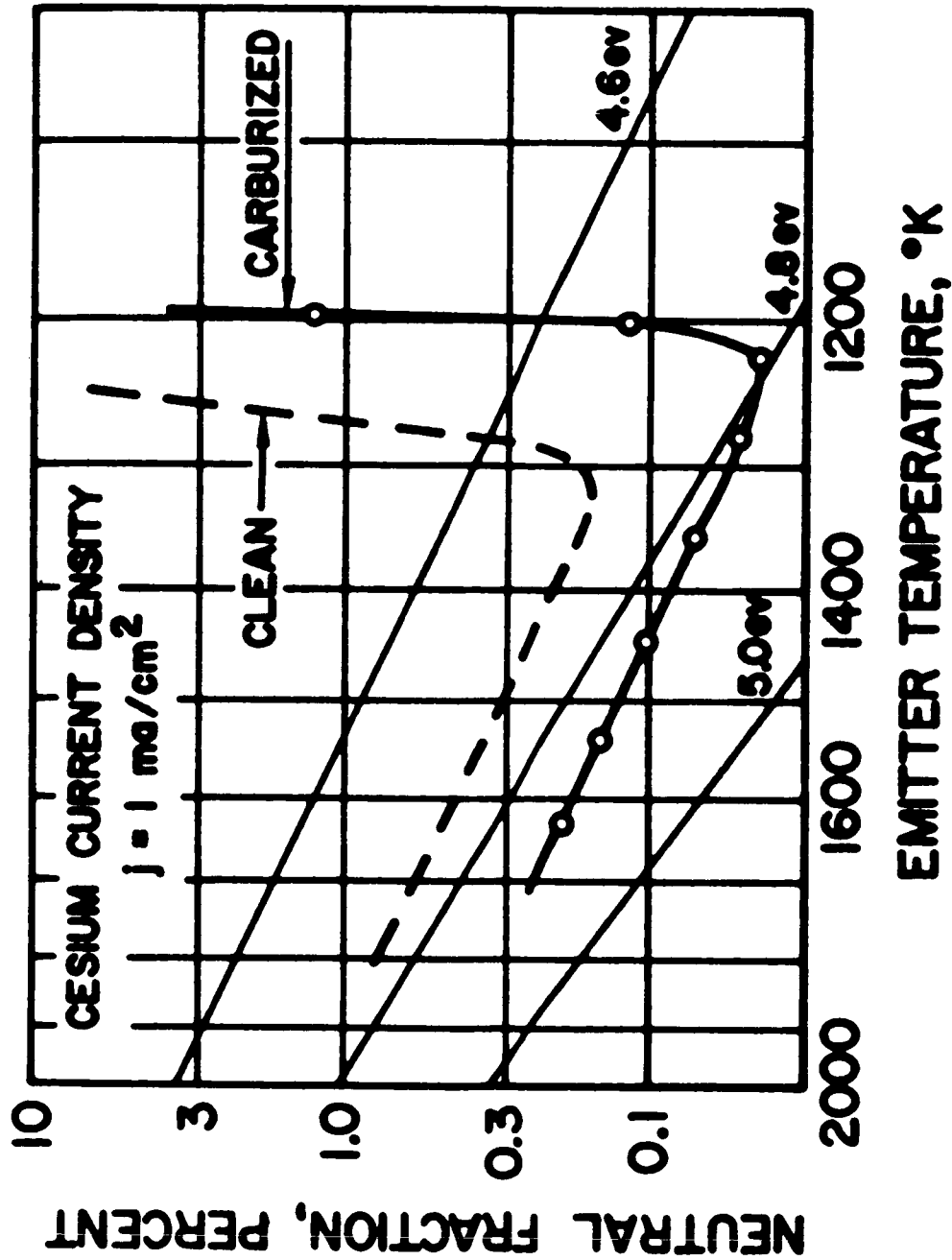


FIGURE 6. CESIUM NEUTRAL FRACTION VERSUS TEMPERATURE FOR CARBURIZED POROUS TUNGSTEN IONIZER

The superior ion emission of tungsten carbide is offset by its higher thermal emissivity. One measurement of a carbided porous tungsten yielded a value of 0.45. Since this value is constant with temperature it is not too much higher than for clean porous tungsten at the ion operating temperatures above 1500°K . Also since the heat lost out of the sides and back etc., is reduced by the lower critical temperature, the carbide surface might be capable of operating at a better power efficiency despite the higher emissivity.

Calcium

These studies have been plagued for years by a low work-function poison that appears on the surface after a period of cesium operation. This poison would not show up in vacuum electron emission measurements, prior to cesium operation. These measurements would invariably indicate an oxygenated surface of over 5 volts work-function. Even with cesium, if the temperature never exceeded 1600°K or so, the poison might not show up. With excessive oxygen conditions (poor vacuum) the poison would not appear. However, improved vacuum and higher temperature allow the poison to appear after operating in cesium for a short period. The standard method of ridding ourselves of this poison was to turn off the voltage (this prevents undue sputtering and raises the cesium coverage throughout the porous tungsten), continue to flow cesium through the porous tungsten, and heat for hours at above 2000°K .

For times after this, traces of the poison might be detected. It would appear on the surface after high temperature operation. At high temperature, although it would arrive at the surface more rapidly, it would evaporate even more rapidly and so have an undetectably low surface coverage.

Repeated attempts to identify this material by optical or X-ray spectroscopy failed. We would know that the material was being evaporated off onto our grid wires because of their electron emission characteristics and the fact that we could reevaporate it onto our porous tungsten and re poison it. The quantity, however, was always too small to detect.

We suspected that the poison might be barium because our porous tungsten manufacturer's main business was producing barium impregnated porous tungsten. When barium was evaporated onto our sources, it proved to be very bad indeed. However, we now believe our poison has been calcium. This material is common - the chief impurity in tap water. Some tungsten manufacturing processes use calcium. Our tests showed calcium acted like our familiar poison. On top of all this, the people who initially sintered our porous tungsten now tell us calcium was one of their main impurities. When they fired the porous tungsten in a hydrogen furnace, the excess hydrogen being burned off, burned with a red flame!

The tests on calcium were mostly qualitative, despite a long period of study. We did not know our calcium arrival rate. Its influence depended on the length of exposure and at what

temperature it was made. After exposure was stopped, the calcium would migrate from the interior and replenish the calcium evaporating from the surface. Severe poisoning would occur and this poisoning would persist for many minutes at temperatures above 1600°K .

Some of the results of the calcium studies are shown in figures 7, 8 and 9. Figure 7 shows the severity of the initial poisoning and the slow decay of the poisoning for a small amount of calcium deposited on the surface. Figure 8 shows the effect on the tungsten work-function without cesium. Figure 9 shows the effect with cesium (the "S" shaped curve.)

It appears that in addition to lowering the work-function and causing more neutrals, calcium increases the binding energy of cesium at some sites and increases the critical temperature and even further reduces the work-function at higher and higher cesium flow rates. Sometimes there is a high pseudo critical temperature (often $>1700^{\circ}\text{K}$), which is the temperature necessary to evaporate the calcium off the surface as fast as it migrates from the interior.)

Silicon, Boron, Chlorine, and Fluorine

In figure 10, the electron emission "S" shaped curve is shown for porous tungsten on which high purity silicon metal was evaporated, operating with a cesium feed rate equivalent to 1 ma/cm^2 . As its chemical similarity to carbon might suggest, the curve resembles that of carbided tungsten. Silicon increases the high temperature work-function (5.1 volts for silicon vs. 4.9 volts for

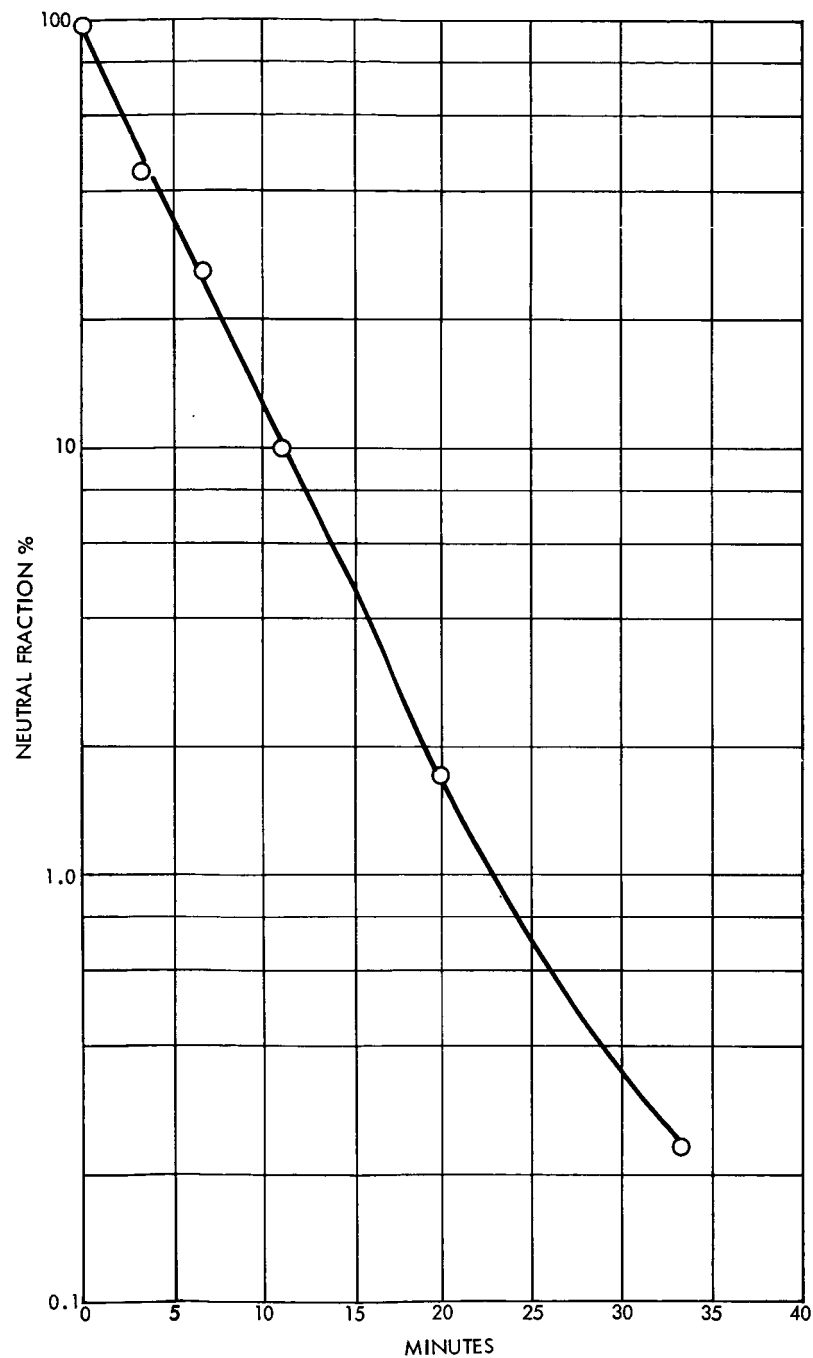


Figure 7. Cesium neutral fraction from porous tungsten versus time after exposure to calcium ($T = 1600^{\circ}\text{K}$, $j = 0.5 \text{ ma/cm}^2$).

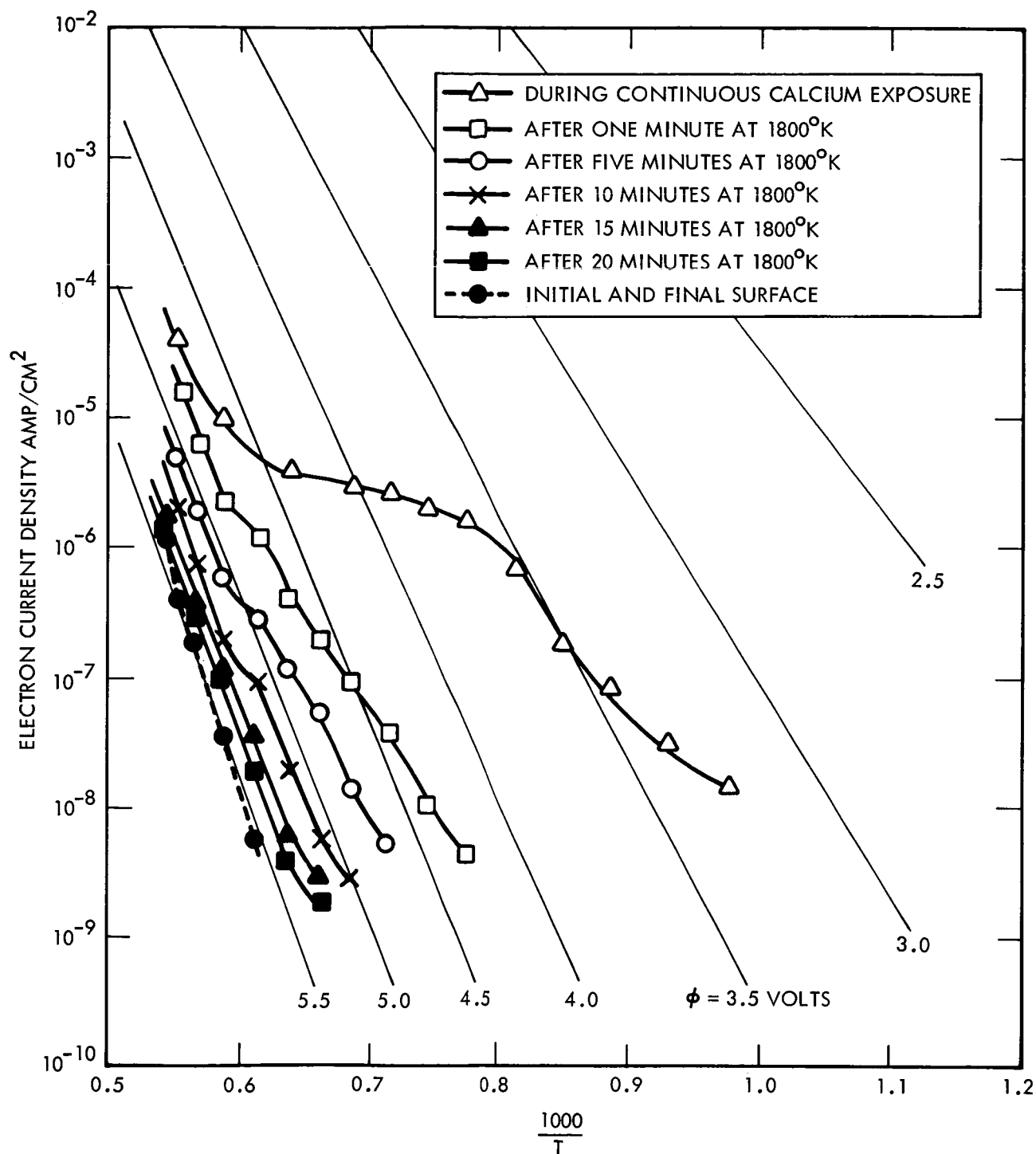


Figure 8. Electron current vs temperature from porous tungsten at varying times after exposure to calcium (with no cesium present).

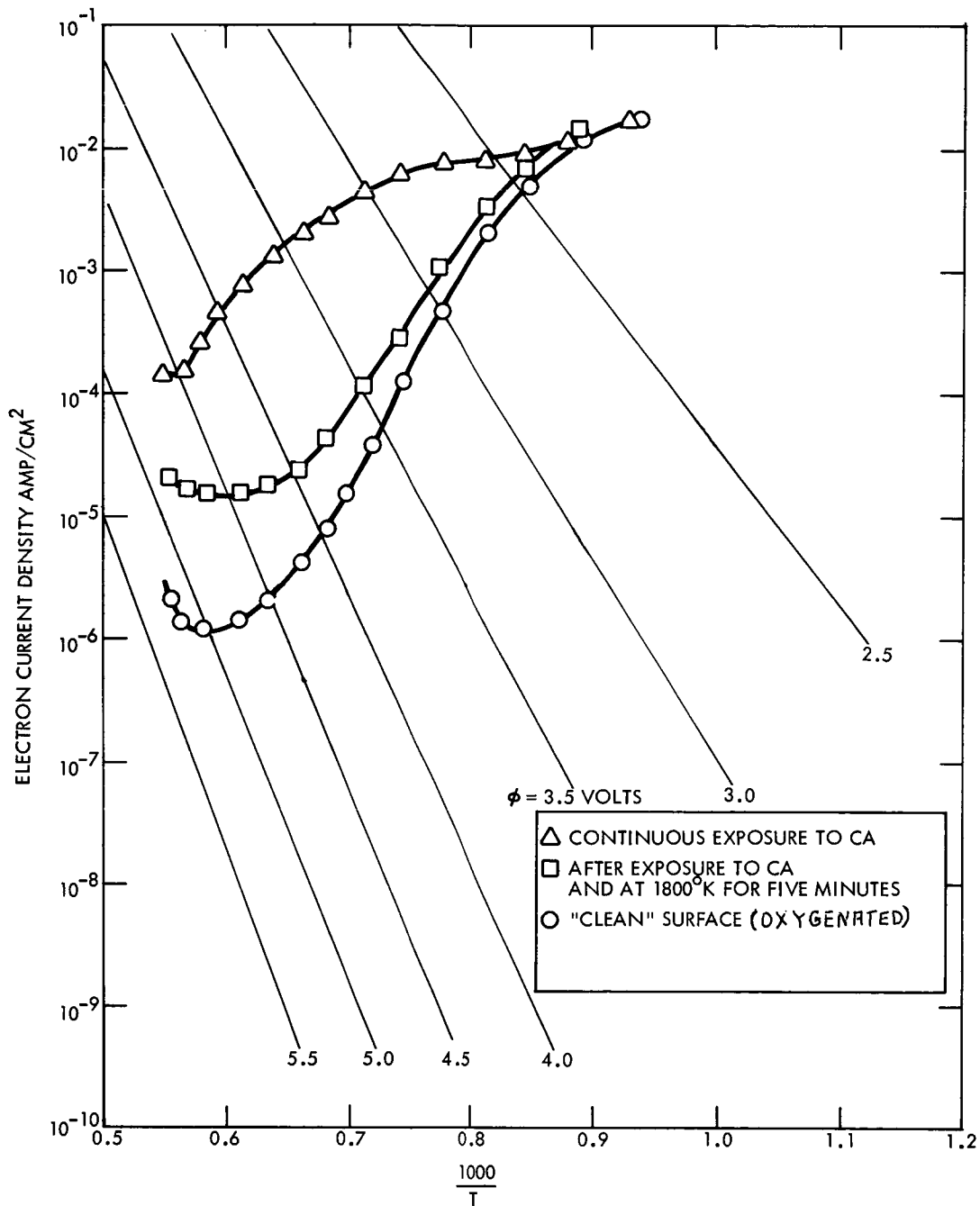


Figure 9. Electron current density vs temperature from porous tungsten in presence of 1 ma/cm^2 cesium under different conditions.

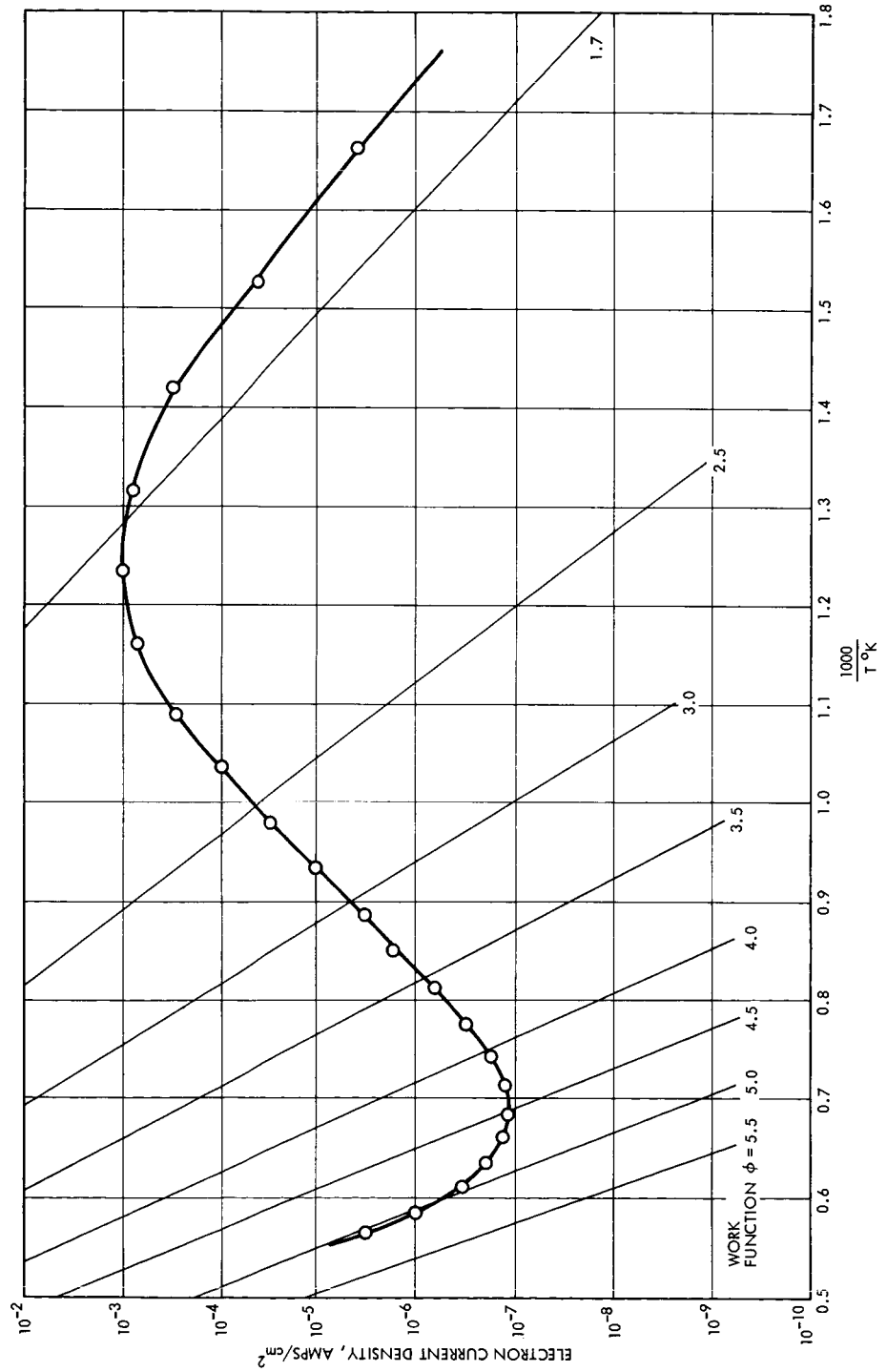


Figure 10 Electron emission "S" shaped curve for porous tungsten ionizer with silicon evaporated on the surface.

carbon), and the minimum is deeper than for clean tungsten. Consistent with this is the observation that porous tungsten with silicon on it is superior to clean tungsten as an ion emitter with essentially the same critical temperature but with approximately half the neutrals. No measurements of thermal emissivity were taken on the porous tungsten covered with silicon. No obvious change was noted.

Silicon is a common impurity in tungsten and was suspected as being a poison. Because of its small affect on ion emission its presence is probably of no significance unless it enters into some chemical compound that can affect the residency of some more important material on the surface.

Boron was investigated because of the suggestion that it might be connected with observed poisoning. It had very little affect on the ion or neutral emitting properties of clean tungsten.

It was observed that chlorine had no affect on the operation of an ion emitter. This is consistent with the finding of M. D. Scheer and J. Fine⁽¹²⁾ who found no difference whether their atomic beam was cesium atoms or CsCl molecules. This is expected, since it is reported in the literature that chlorine completely desorbs at ion operating temperatures. This observation means that a metal whose deposition is to be studied can be evaporated onto the tungsten as a chloride, if the chloride is sufficiently volatile and obtainable in high purity without introducing side effects due to the chlorine.

Fluorine does not lead to poisoning of any sort. It was suspected that it did. It acts like oxygen - lowers the neutrals and raises the critical temperature. The most successful method of depositing fluorine is by the direct evaporation of CsF.

CLEAN TUNGSTEN DATA

Achievement of a Clean Surface

For nearly two years we were unable to achieve a clean surface because of the presence of contaminants, our inexperience, and our limiting vacuum. Even after acquiring a sufficiently good vacuum to maintain a clean surface, it was many months before we produced a clean tungsten surface even though the porous tungsten had been heated at 2000°K for hours. A clean surface was first produced by sputtering. Our first clue to the usefulness of sputtering came through cases of inadvertent sputtering cleaning up our poison. At one period a mystery was the improvement of operation by applying higher voltage. Soon the effect of electric field was ruled out, because an increase in the negative voltage on the accelerating grids would not affect the improvement. It soon became apparent that the improvement was caused by sputtering from negative ions, (probably negative copper ions⁽¹³⁾) that would penetrate through the grid wires when insufficient negative voltage was applied to the grids compared to the positive source.

Another case of inadvertent sputtering was discovered to be the cause of limiting the high electron current peak of the "S" shaped curve when, say the oxygenated surface was being studied. It turned out that at the very high electron currents, the accelerating grid wires were being electron bombarded and heated above critical temperature. Consequently cesium evaporated from the porous tungsten, upon hitting the hot grids, were converted to ions and were accelerated to the negative porous tungsten, sputtering off the oxygen that was responsible for the high current, etc. The use of the heated upper grids to produce ions which would sputter the negative porous tungsten became our prime tool. We used sputtering to clean off remnants of poisons or oxygen. (This tool was possible because of the flexibility of the accelerating system used with the one-inch-diameter sources. This accelerating system was two sets of tungsten grids, each of which could be heated up under operation⁽¹⁴⁾.)

Cleaning by sputtering is illustrated in figure 11 where oxygenated W is cleaned up after 30 minutes of sputtering. The accompanying ion emission curves are shown in figure 12. Curve A is heavily oxygenated (as if the source had been exposed to oxygen recently but no oxygen pressure was present at the time of measurement) and there was an increase in critical temperature as would be predicted from the figure 11. Figure 13 indicates the rate that oxygen migrates back onto the clean surface after sputtering has ceased. Note the obvious sign of oxygen. After a few minutes the work-function is higher and the cesium coverage is increased as the

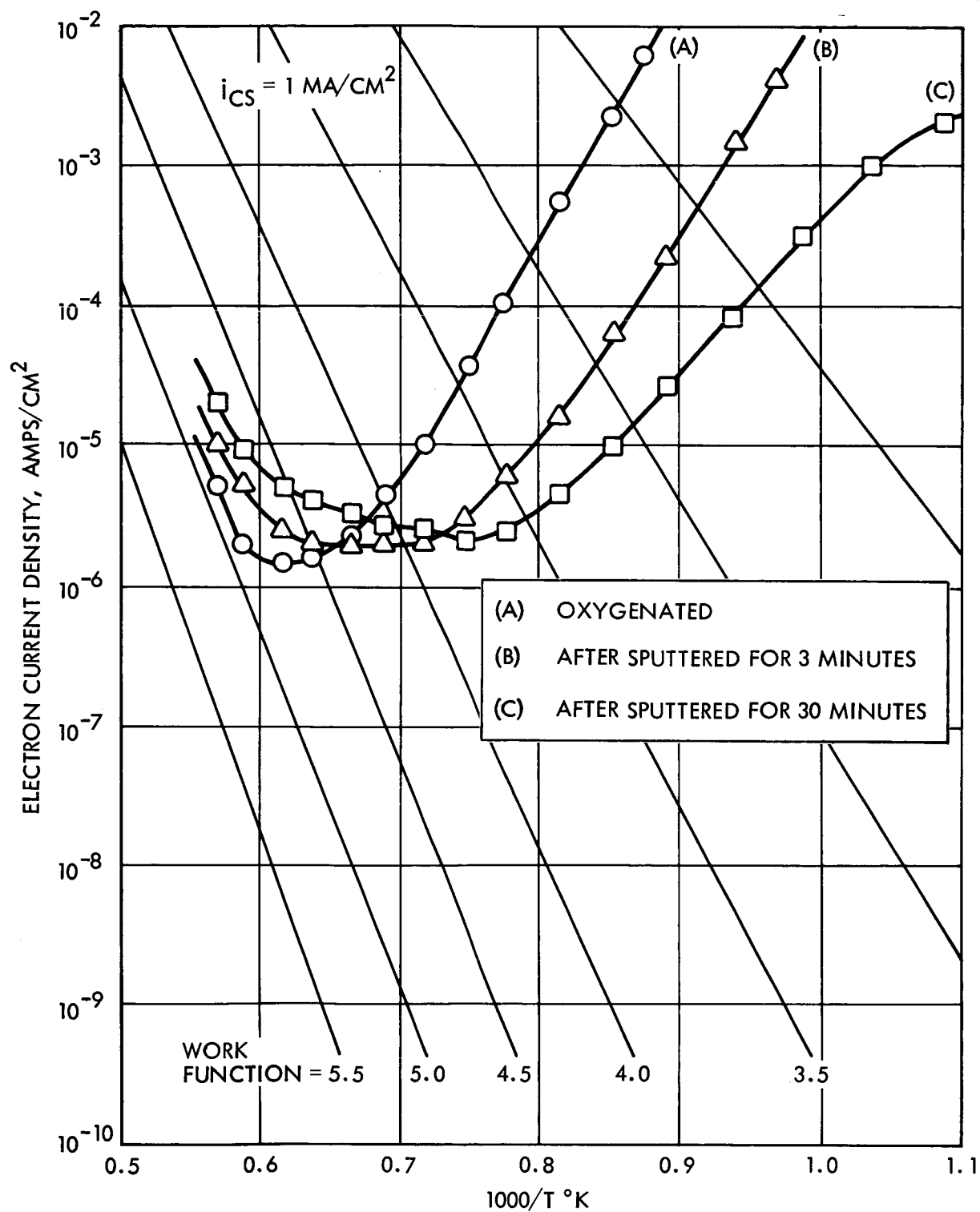


Figure 11. Electron emission "S" shaped curves from porous tungsten in cesium (1 ma/cm²) as oxygen is removed by sputtering.

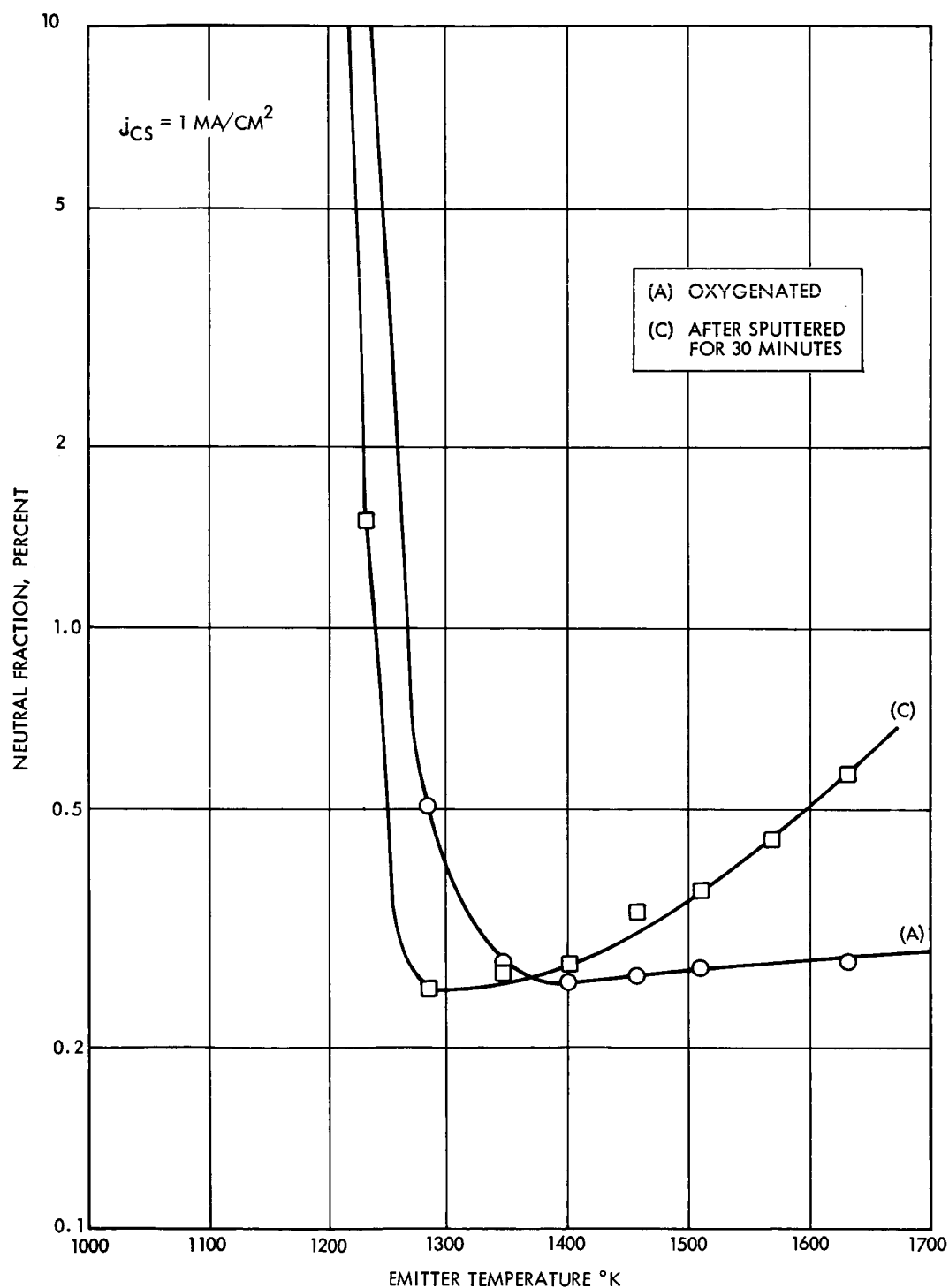


Figure 12. Cesium neutral fraction versus temperature from a porous tungsten ionizer oxygenated (A) and sputtered clean (C).

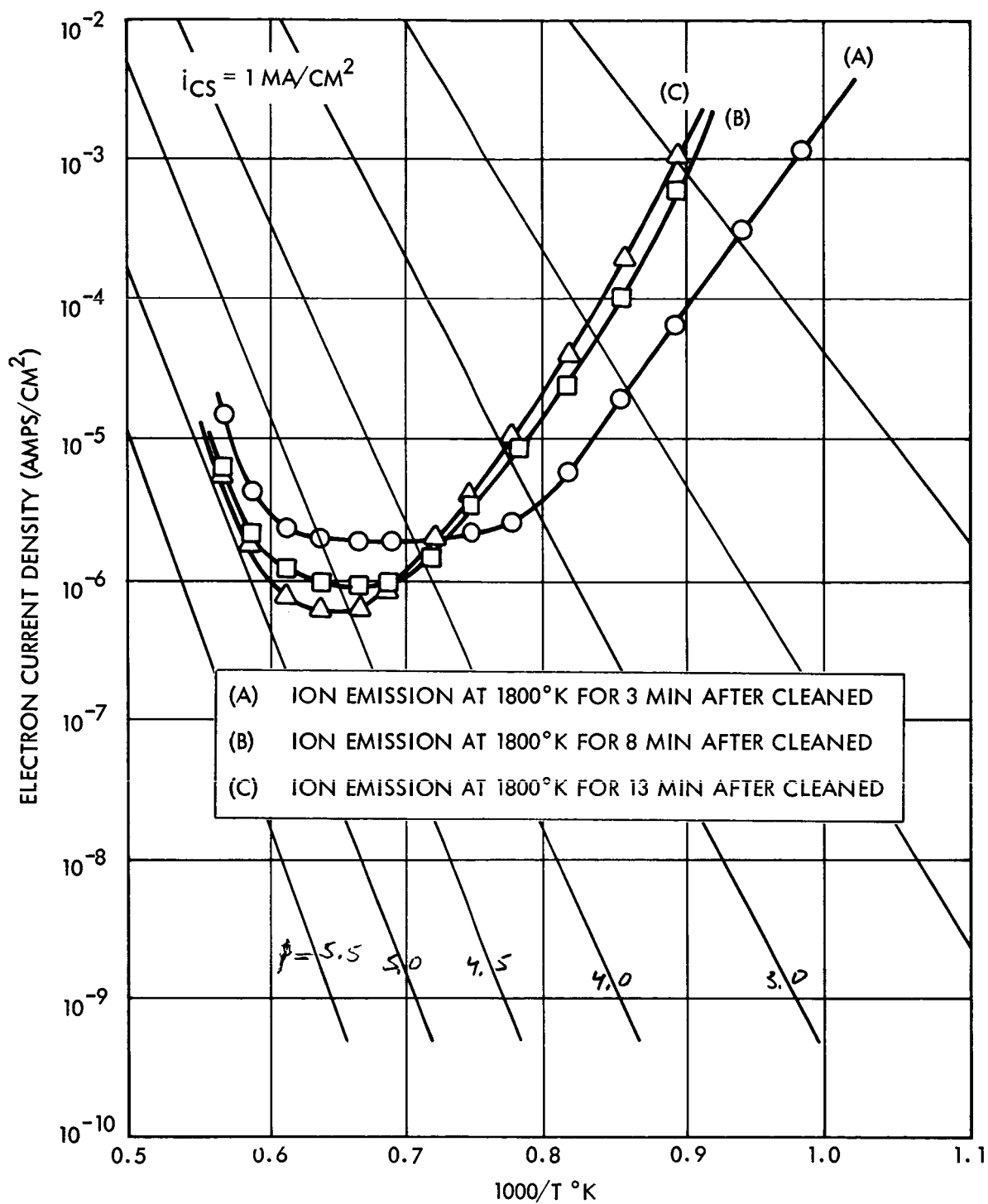


Figure 13. Electron emission "S" shaped curves from tungsten in cesium (1 ma/cm^2) as oxygen returns after sputtering.

temperature is decreased. However, the degree of oxygenation is still very slight and our 3.7 volt rule would predict negligible shift in critical temperature. Figure 14 shows the accompanying ion emission curves. All curves have the essential features of clean tungsten.

"S" Shaped Curve

As we have seen in many previous instances, the electron emission "S" shaped curve can more accurately identify a surface than the ion emission characteristics. In figure 15 we see the "S" shaped curve for clean tungsten operating in a cesium flow rate equivalent to 1 ma/cm^2 . As always we have the electron emission expected from surfaces of constant work-function calculated from the Richardson equation with $A = 120 \text{ amps/cm}^2 \text{K}^0$ superimposed on the graph so that the work-function of the cesium covered surface can be read off at any temperature. The clean tungsten has a high temperature bare work-function of 4.7 volts. The depth and width of the valley is an identifying feature of clean tungsten. Also we have come to expect a minimum to maximum ratio of about a thousand at this current density. The 3.7 volt rule predicts a critical temperature of about 1300°K .

Neutral Fraction Versus Temperature

Figure 16 shows the cesium neutral fraction versus temperature for the clean tungsten operating at 1 ma/cm^2 current density. The sharp break is at the critical temperature of

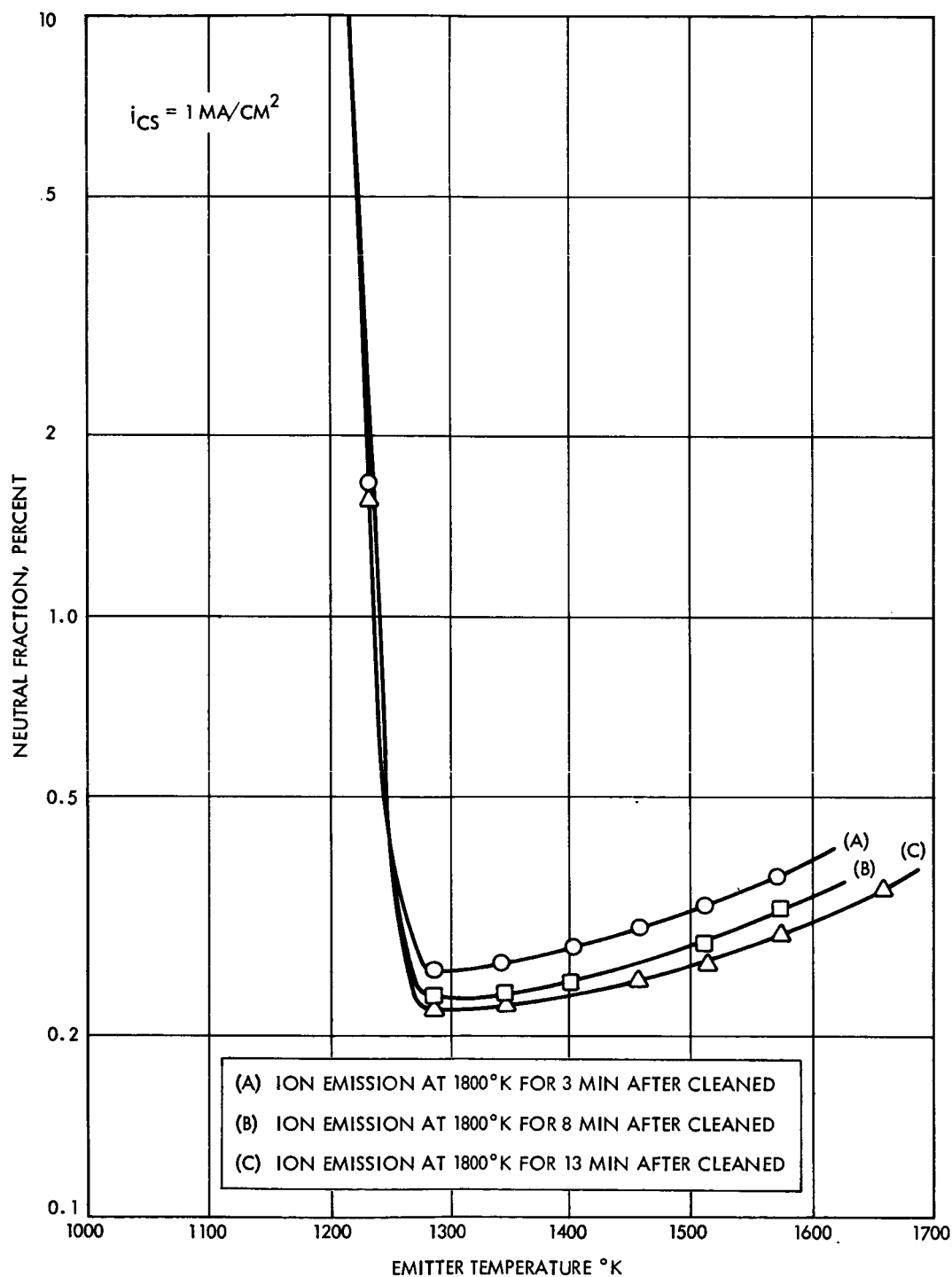


Figure 14. Cesium neutral fraction versus temperature for porous tungsten in conditions shown in Fig. 13.

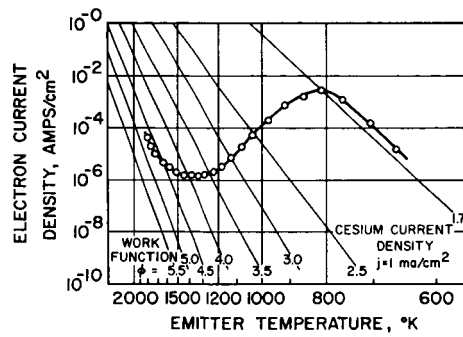


Figure 15. Electron emission "S" shaped curve for clean porous tungsten ionizer.

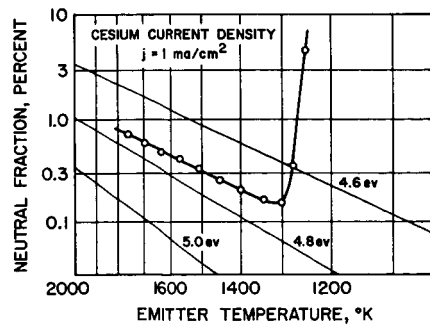


Figure 16. Cesium neutral fraction versus temperature for clean porous tungsten ionizer.

slightly less than 1300°K . Operations above the critical temperature produce more neutrals (the same ion current) according to the Saha-Langmuir equation $f(\%) = 100 \left(1 + \frac{1}{2} \exp \left(\phi - 3.9 \right) / KT \right)^{-1}$. The neutral fraction, f , predicted from this formula is plotted in this curve as straight lines. More perfect correlation with theory could hardly be asked for. In this case where the surface coverage remains low as the temperature is lowered towards critical temperature, the work-function can be inferred from the neutral fraction. This is not true at higher current densities or for oxygenated tungsten.

Neutral Fraction Versus Ion Current Density

The excellent agreement with theory at 1 ma/cm^2 indicates that the porous nature of the surface is not affecting the results. We would therefore expect the same result (if the temperature is held constant and above the critical temperature at the highest current density to be measured) at lower current densities. This is true and seen in figure 17. At higher current densities the neutral fraction increases. In this section we are discussing the operation at low current densities. Later we will treat the effect of the pore distribution at the surface on the neutral fraction at high ion current density.

Critical Temperature Versus Current Density

In figure 18 is shown the critical temperature for clean

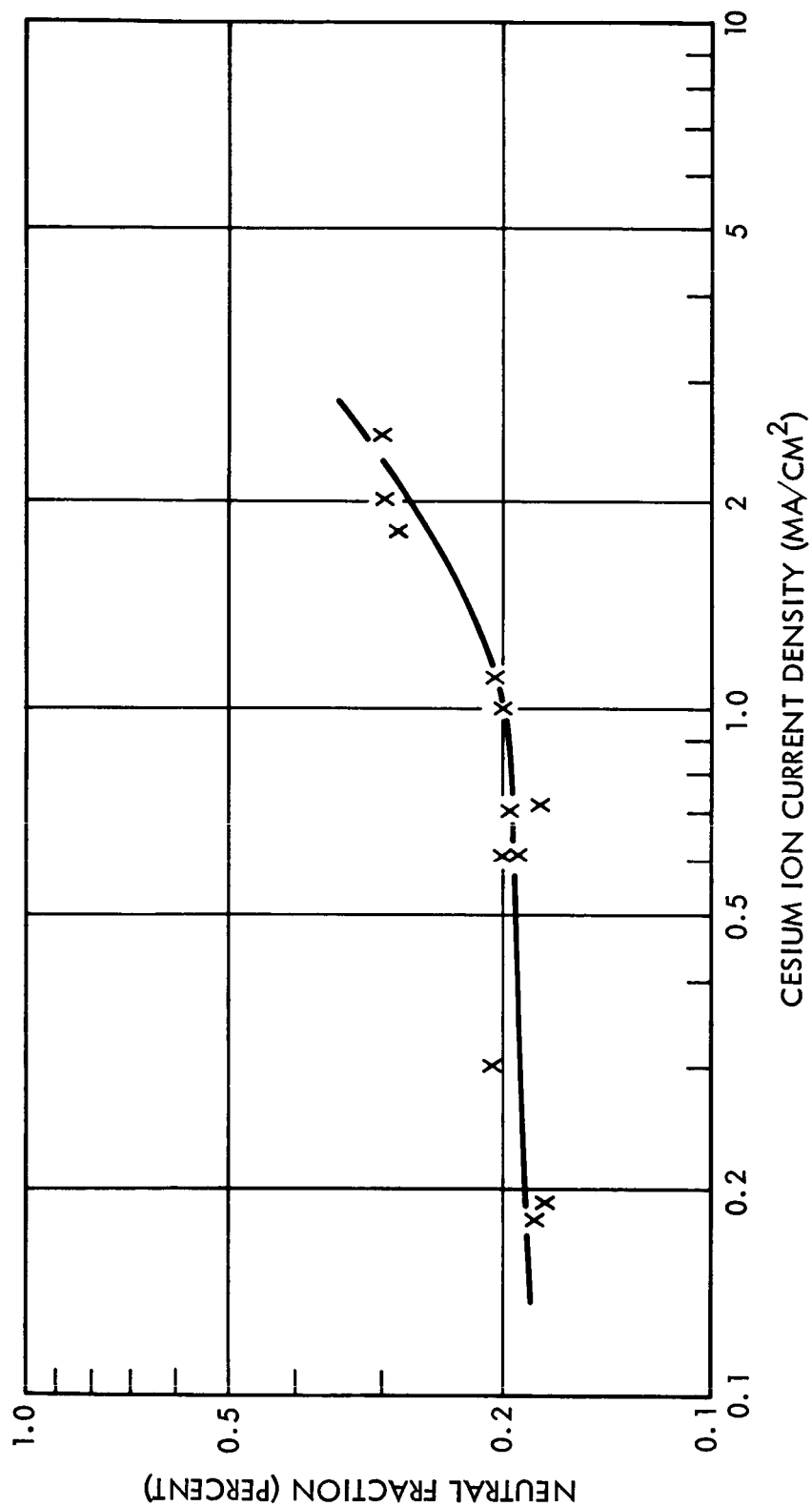


Figure 17. Cesium neutral fraction versus ion current density from clean porous tungsten.

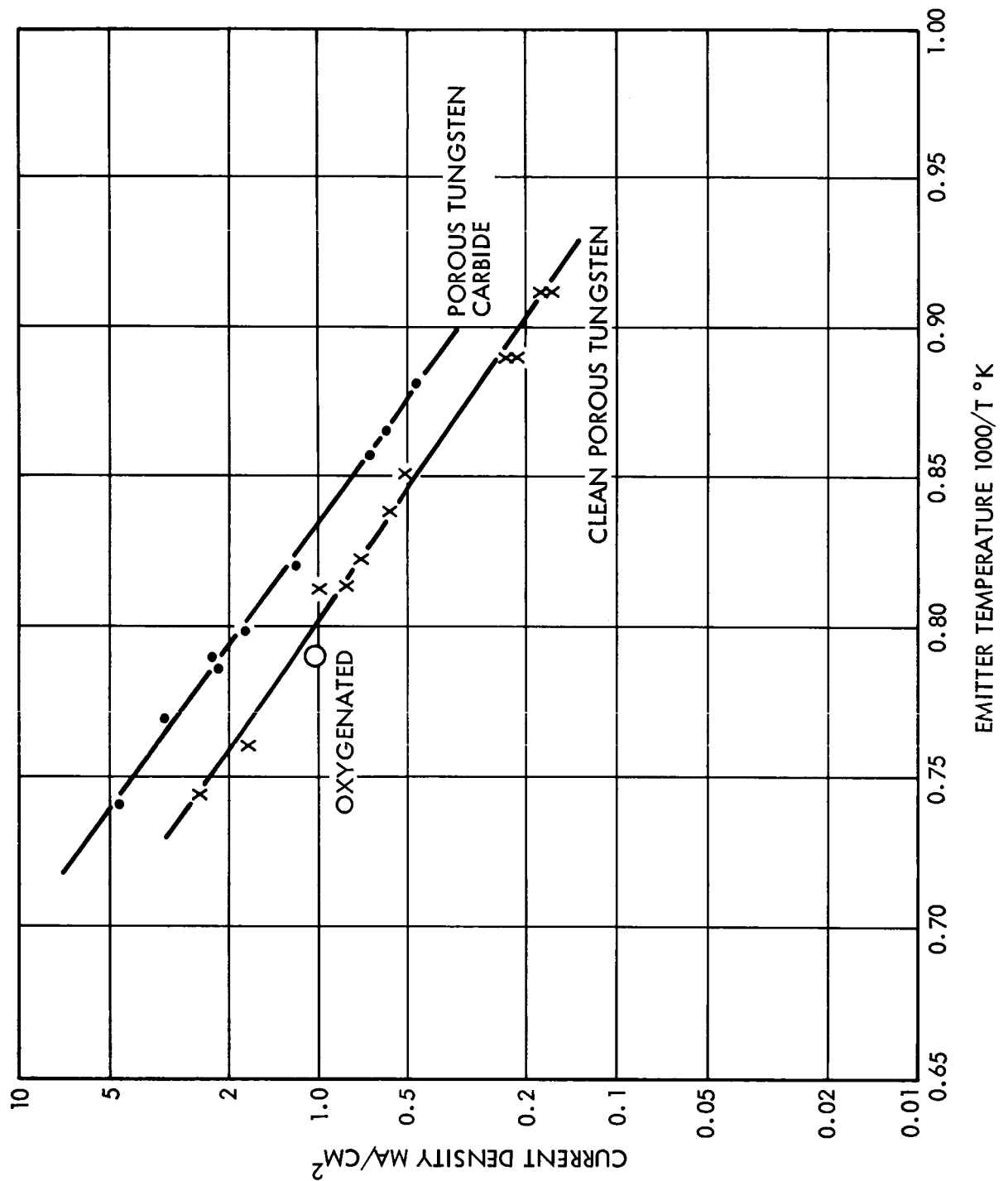


Figure 18. Critical temperature of porous tungsten versus cesium ion current density.

tungsten at different ion current densities with the data for carbided porous tungsten shown for comparison. Oxygenated (weakly with negligible oxygen pressure) tungsten at one current density is also shown. Straight lines are drawn through the data points. The slope does not agree with anyone's predictions. The lines shown have a slope of about 1.3 volts. Analysis and data by us⁽¹⁵⁾ in the past indicate that for solid tungsten the slope should be 2.2 volts. Analysis⁽¹⁶⁾ of I. Langmuir's data gives 2.85 volts. T. Reynolds predicts a slope of about 2.5 volts. M. D. Scheer and J. Fine⁽¹²⁾ find an ion lifetime to have a slope of 2.04 volts. This observed lower slope predicts higher critical temperatures at the higher current densities of interest in ion engines than previous theories relating to solid tungsten would predict.

CHARACTERIZATION OF THE POROUS TUNGSTEN

These previous data taken at low current density were from one-inch-diameter porous tungsten discs, 0.030" thick brazed into a molybdenum assembly that included plenum chamber, heater imbedded in Al_2O_3 , and feed tube. The porous tungsten was sintered, machined and brazed by Semicon of California, Inc., at Watsonville (the operation has been disbanded and some personnel has formed Spectra-Mat, Inc., Freedom, California, and others have joined the parent company, Semicon of Lexington, Kentucky). The methods used were proprietary. Our best information is that:

(1) sintering was above 2000°C for about a few hours in hydrogen (probably wet) using non-sorted angular 4-5 micron diameter powder, (2) machining was fine cuts on the lathe with the pores filled with acrylic plastic polymerized in the pores followed by firing in wet hydrogen to evaporate and decompose the plastic and burn out any resulting carbon, (3) brazing with unknown materials was done in hydrogen. (the later sources were heliarc-welded.)

The resulting porous tungsten was about 80% dense, had a shiny surface with a low total hemispherical thermal emissivity, and would have a transmittivity if 1 cm thick of about 0.3×10^{-5} . The observed pore size and distribution was never analyzed in detail. We felt bulk properties as determined by metallographic preparation and certain other methods of analysis were of little use. We are interested in the manner the pores emerge onto the surface which is tested. We would make the tests on the surface as received or altered by mild sputtering and oxydation. The as-received surface as studied under the microscope had open cracks surrounding the flat-topped single crystal particles rather than holes. This possibly resulted from the resintering of the surface burnished by machining during plastic removal and brazing. The surface appearance was compatible with the size particles (4-5 μ) used which would produce about 4×10^6 particles/cm².

The following higher current density data were taken on 5/32" diameter, 0.020" thick porous tungsten discs manufactured by Philips Metalonics and Electro-Optical Systems, Inc. Philips Mod A porous tungsten has a stated (by manufacturer) mean pore diameter

of 4.3 microns, has a pore count of $0.7 \times 10^6/\text{cm}^2$ and unknown transmittivity. Philips Mod B has a stated mean pore diameter of 3.6 microns. Philips Mod C has a stated mean pore diameter of 2.1 microns, a pore count of $2.3 \times 10^6/\text{cm}^2$ and an estimated transmittivity thickness product of $1 \times 10^{-5}\text{cm}$. E.O.S. E-6 porous tungsten has a stated average pore size of 0.9 micron, density of 81%, open pore count of about $2 \times 10^6/\text{cm}^2$, a transmittivity thickness product of $0.85 \times 10^{-5}\text{cm}$ corrected from a measured Knudsen leak rate with helium of 0.55 cc/sec. (This is a Knudsen permeability of $1.55 \times 10^{-7}\text{ gm cm}^{-1}\text{ sec}^{-1}\text{ torr}^{-1}$ to air).

PROGRAM TO ACHIEVE HIGH CURRENT DENSITY

Experimental Limitations

The one-inch diameter porous tungsten with a fine tungsten wire accelerator assembly could be run at $10\text{ ma}/\text{cm}^2$, only with difficulty. The insulation was marginal at high voltage. The electrostatic attractions between the fine wires would cause them to attract together and short, especially when they were being heated during operation at high voltage. Also the large area (5 cm^2) made the power consumption excessive - taxing our power supplies and making cooling and outgassing problems more severe.

Along with the program to study a porous tungsten material made by a range of manufacturers, we wished to increase the current density capability. The result was the adoption of 5/32" diameter porous tungsten mounted in a Pierce angle cone facing a

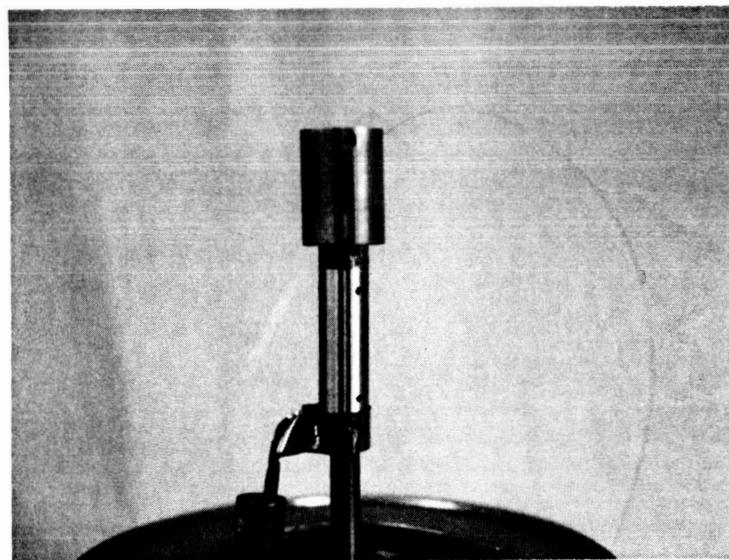
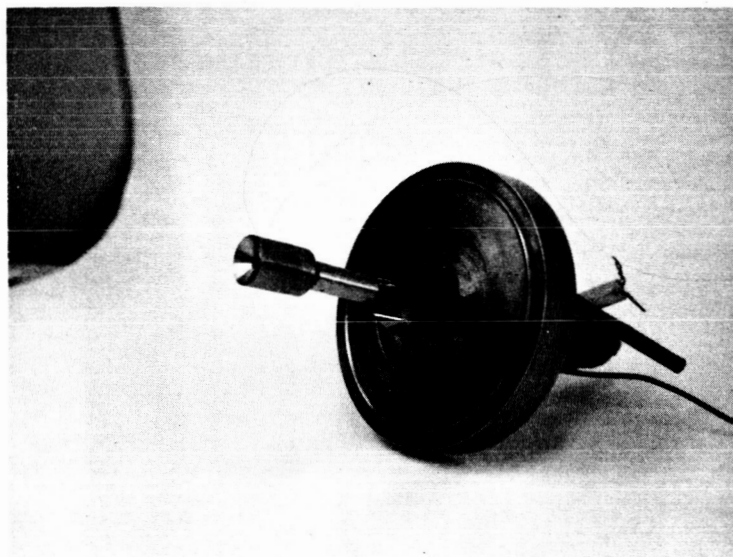


Figure 19. Photographs of the assembly to mount and heat $5/32$ " diameter porous tungsten pellets.

copper accelerator with an aperture of source diameter one diameter away. (Figure 19) This system had a much greater effective accelerating distance (.075" in the old system to 0.160" in the new system) so that much higher voltages would be required to get even the same current density. The voltage insulation was improved accordingly.

This assembly allows easier operations to 10 ma/cm^2 . We have extended the measurement to 16 ma/cm^2 . However at times we are seriously bothered by huge electron "drain" currents from the accelerator electrode to the source. These currents and how they are to be eliminated by applying the accelerating field with an electrode in the plane of the emitter are discussed in a later section.

Effect of Accelerator Structure on Neutral Measurements

In order to unambiguously measure the neutral fraction leaving the tungsten surface (not the neutral fraction escaping from the engine), and in order to preserve the simple calibrating procedure of turning off the voltage, we made our acceleration electrode very open. The central aperture was surrounded by 6 similar apertures. This presented as little scattering area as possible to the neutrals. Serious error can result from improper interpretation of the neutral measurements when a large amount of scattering is present. To help illustrate this important point, let us consider a sufficiently ideal case that we can see the answer and one that approaches an actual situation. Consider an ion

engine of the STL concept - a large continuous surface of scallops with accelerating bars over the intersection of the scallops. For illustrative purposes, let the bars be infinitely thin, be 50% of the total area, and be far from the emitter compared to the bar separations. Let us use two detectors to measure the neutrals; (A) looks at neutrals coming from a large area, (B) can look through the bars and sample the density of neutrals leaving the surface. We now apply a cesium feed rate and take off the grid. We will set the two detectors to read 100%. We now replace the grid, but apply no voltage. (A) will again read 100% as the same total amount of cesium must eventually get out of the grid. The assumptions we made will assure that the resulting distribution will be the same. Detector B, however, will read 200%, since in order for 100% to get out 50% of the area, the surface density must increase by two. Now apply voltage. Because of the temperature, work-function, and pore distribution, let the neutral fraction be 4%. Of course all the ions get out of the holes; however; of the 4% neutrals, half are scattered by the grids and returned back to the surface and to first order can be considered to all make ions which are transmitted out of the system. Detector A will read 2%, Detector B will read 4%. However, both will read 2% of the previous voltage-off reading. Operators of both instruments are justified in saying that this 2% represents the mass utilization of the engine, but it is difficult for them to correct this 2% to find the real 4% neutral fraction from the surface. We directly measure the 4% by eliminating the scattering.

In cylindrical geometry it is easy to magnify the problem. A single aperture of diameter, D , in a solid plane a distance, D , above a disc of diameter D , emitting with a cosine distribution passes less than 20% of the emitted material. If the aperture diameter is 70% of the emitting disc, the amount passed is reduced by another factor of two. Then only 10% of the neutrals would get through without scattering; the other 90% would scatter backward and have to make another attempt at getting out as an ion or neutral. In such a situation, the neutral detector should be calibrated to 100% with the accelerator off. The reading with accelerator and voltage on will be, say 4%, the neutral fraction*, the thing we feel one should discuss when studying surfaces. When the voltage is off, the neutral detector might read 300%. This is very understandable. However, if the voltage-off reading were called 100%, the voltage on reading would be called 1.33%, which indeed is a measure of the mass utilization, but not the neutral fraction. In an ion engine, where charge exchange in the acceleration region is of vital concern, it is the neutral fraction again that is of concern. A scattering accelerator, although increasing the mass utilization, increases the charge exchange problem by scattering the neutrals into the accelerating region.⁽¹⁷⁾

If some of the surface that the neutral detector sees is a scattering surface, and this surface is capable of emitting ions with the voltage applied, the situation is far more complex.

*If the emitter area seen by the detector is not reduced by the aperture.

The " Ω " Field Accelerator

The demand for testing at higher ion current densities has forced us to consider another testing geometry. The main requirement was the complete elimination of drain current problems, increase in perveance if possible, and open structure for the ease of detecting neutrals and the ease of sputtering. Desirable also, would be the lack of a hot focusing electrode from which electrons could come and confuse the "S" shaped curves.

These conditions are met beautifully in the " Ω " field accelerator where the accelerator electrode is in the plane of the emitter. No material from the accelerator can get on the emitter, so it can be made of a refractory metal and heated to remain itself clean. Also, it should intercept no cesium - therefore, no drain current problems on both counts. There is no dispute about the openness of this structure. There will be a slight lip surrounding the emitter disc which will smooth out the field on the surface, give a concave shape to the close equipotentials, and launch the ions slightly inward. The chosen geometry and the space-charge free equipotential are plotted in figure 20. An estimated ion trajectory is sketched on the figure.

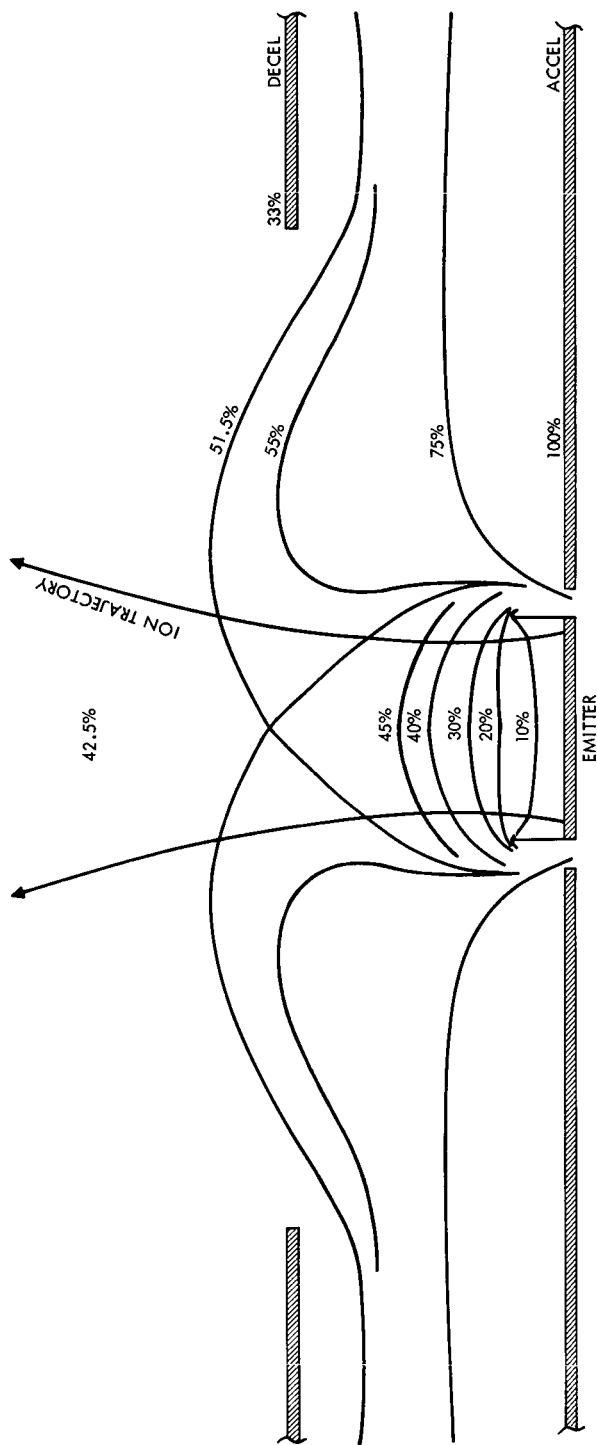


Figure 20. Space-charge-free equipotential plot of the "Ω" field accelerator system. Ion trajectories are only schematic.

Computer Studies of the "Ω" Field Accelerator

Computer studies are in progress on this geometry using a program furnished us by NASA.⁽¹⁸⁾ The programs have to be altered to account for the differences in the two computing systems. The basic program is different than the two dimensional program that finally, after about a month, yielded proper answers. The big difference lies in the cylindrical geometry - not the unusual electrode geometry. In figures 21 and 22 are seen the solutions for one trial geometry. In figure 21 the ion trajectories and equipotential lines are shown for the space-charge-free condition. The ions leave a positive 3300 volt emitter and are accelerated mainly by the field due to the negative 6700 volt accelerator in the emitter plane into zero volt space through a zero volt aperture, the edge of which is slightly off the figure. The position of the 3000 volt equipotential relative to the emitter surface indicates the uniformity of emission. In the space-charge-limited case in figure 22, the spacing of this 3000 volt equipotential line (300 volts more negative than the emitter) indicates the current density that can be drawn. This calculates out to be 18 ma/cm^2 if the current density were constant at its maximum value. The computer says the average current density is 17.3 ma/cm^2 . The ion trajectories are very reasonable. In actual practice, the emission will be restricted by the braze to even a smaller area than that for which ion trajectories are shown.

High Current Density Ion Emission

Surface migration is relied upon at low current density

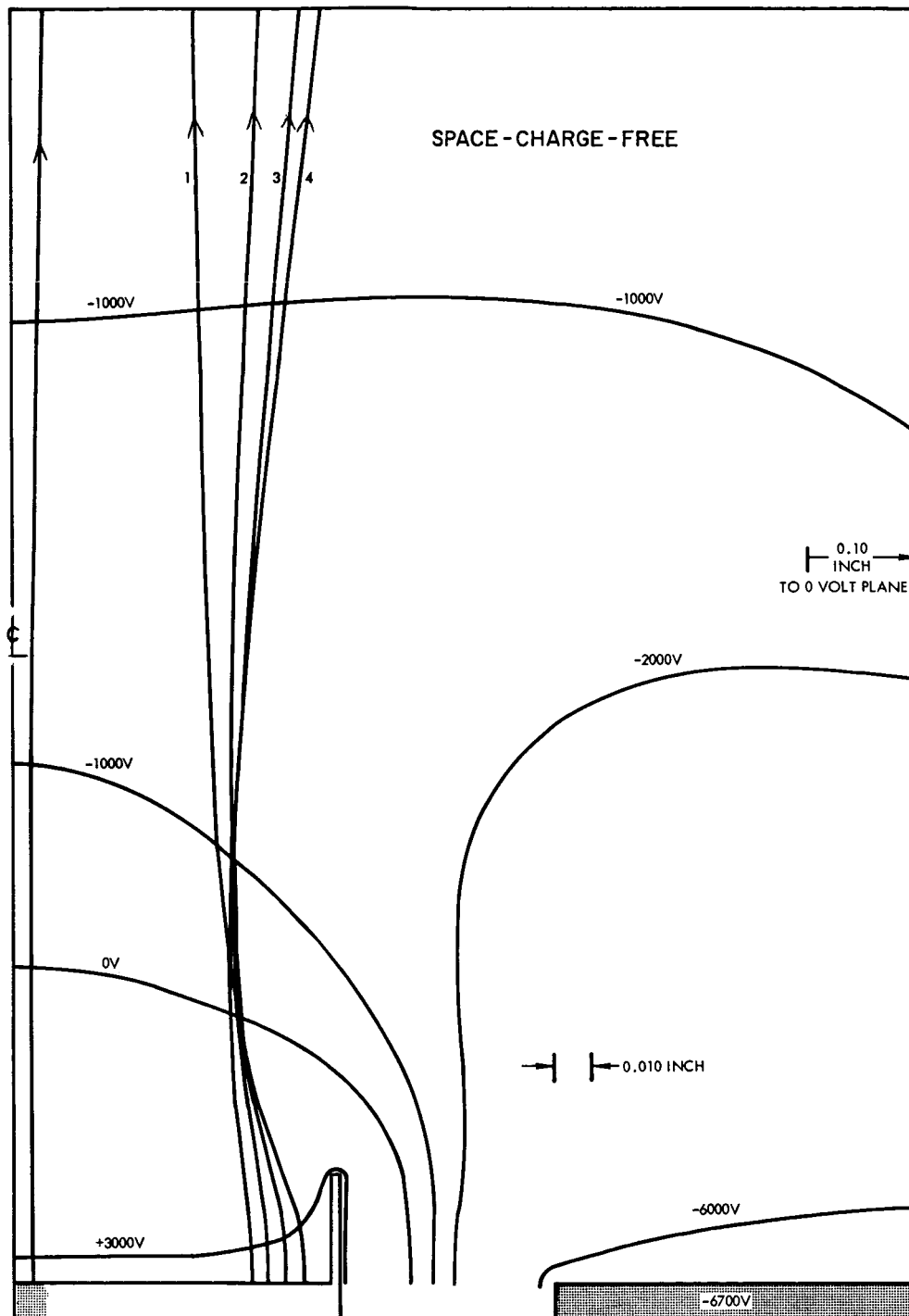


Figure 21. Space-charge-free equipotentials and trajectories for the "Ω" field geometry from the computer.

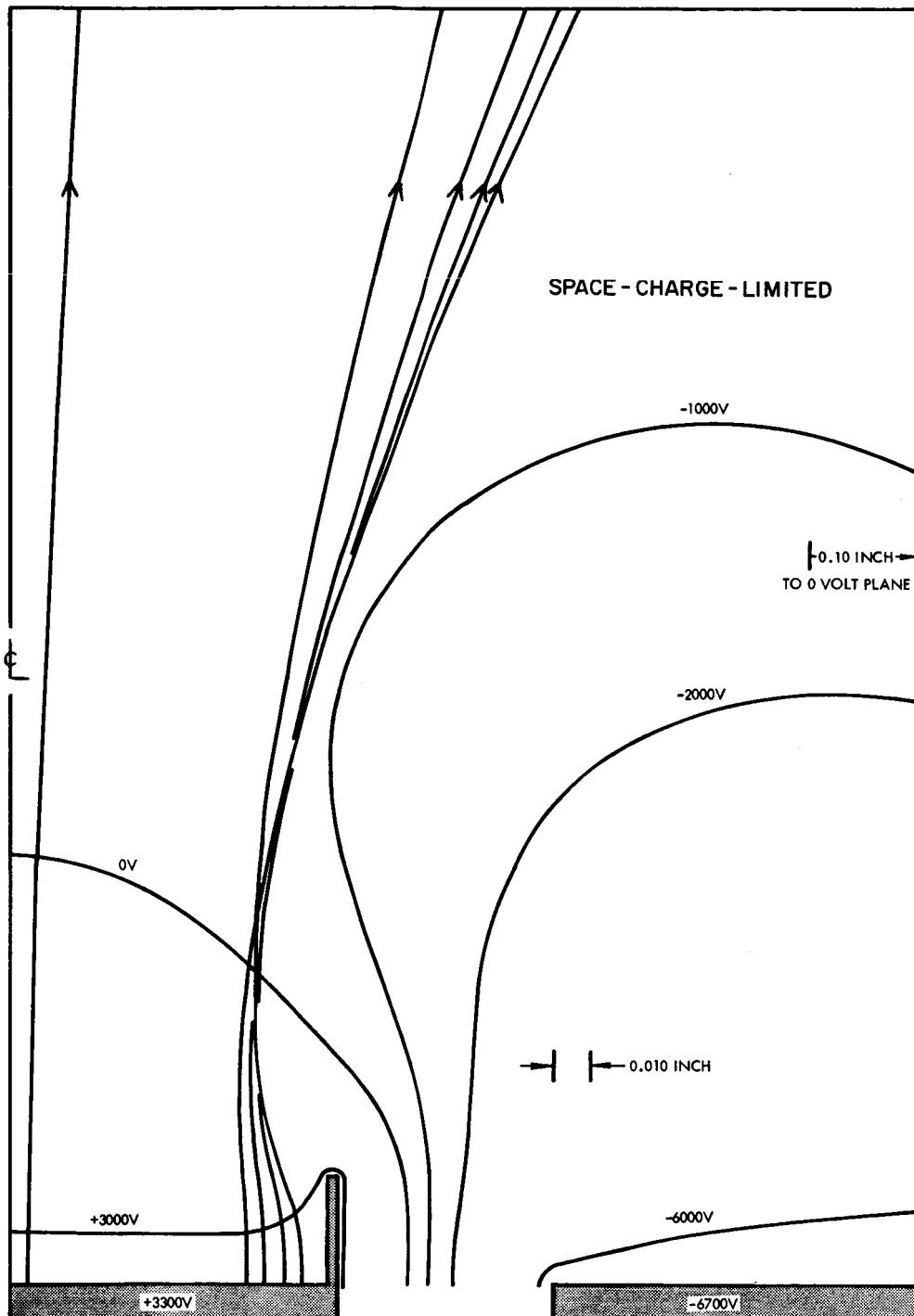


Figure 22. Space-charge-limited equipotentials and trajectories for the "Ω" field geometry from the computer.

to deliver cesium to a position on the surface or near the exits of the pores where sufficient electric field exists to allow ions to leave. As more ions are demanded, the surface concentration gradient is forced to increase - and produce more neutrals. Many detailed treatments^(19,21) of this problem exist. Let us however proceed only so far as to see why there might exist a problem. The surface diffusion coefficient of cesium on tungsten is felt to be about $4 \times 10^{-4} \text{ cm}^2/\text{sec}$. and to vary only slowly in the temperature range of interest. Let a pore of radius r exit onto the surface. Let the coverage be 0.1 monolayer one' diameter down the pore walls. This is the largest that the coverage would get even with the voltage off. If any closer to the surface, the neutrals from such a pore would exceed 10%. There then is a limited gradient of surface coverage $\frac{d\sigma}{dr} = \frac{4 \times 10^{13}}{2r}$. The number that could migrate out of the hole would be $D \frac{4 \times 10^{13}}{2r} \times 2\pi r = 5 \times 10^9$ particles/sec. independent of pore size. This is equivalent to a little less than 1 nano-ampere per pore. Should a surface have 10^6 pores per cm^2 , we then would expect trouble with $1 \text{ ma}/\text{cm}^2$ current density and over. (21)

This degradation of the operation is illustrated by the two dotted lines in figure 4. Here at $5 \text{ ma}/\text{cm}^2$, the critical temperature is not sharp. A decrease in neutrals is observed up to temperatures much higher than what should be critical temperature. At $10 \text{ ma}/\text{cm}^2$ the situation is much worse. These tests were for Philips Metalonics⁽²⁰⁾ Mod. C porous tungsten made from graded fine angular tungsten powder.

Surface Etching to Improve Ion Emission

In figure 23 the neutral emission of Philips fine and coarse grain tungsten are compared to 10 ma/cm^2 . The coarse grain is impossibly bad at this current density. An improvement was effected by electrolytically etching the surface. Figure 24 shows the neutral fraction vs. ion current density taken at 1800°K . The fine grain materials look tolerably good with 1% neutrals at 10 ma/cm^2 . However, when one looks back and sees the temperature that must be used to get this 1%, one sees the advantages of increasing further the pore count by using fine powder, or further opening the surface by etching.

We studied two further cases of etching. We tested Philips Mod B and it had characteristics between Mod C (fine-grain) and Mod A (coarse-grain). Etching improved its operation. In testing EOS E-6 material, manufactured from medium-fine graded spherical powder, we achieved vastly superior results after etching. In this case etching significantly increased the permeability of the sample, indicating that the surface had been almost completely "plugged up".

The need for etching might arise because of the cold work that is done on the surface during machining, grinding or polishing. These operations appear to smear tungsten and form bridges over the open areas. This altered tungsten rapidly sinters to an equilibrium condition when heated in the vacuum distillation of the copper, or in the initial heating upon putting into operation. Unfortunately, this equilibrium condition might result in stoppage of the pores

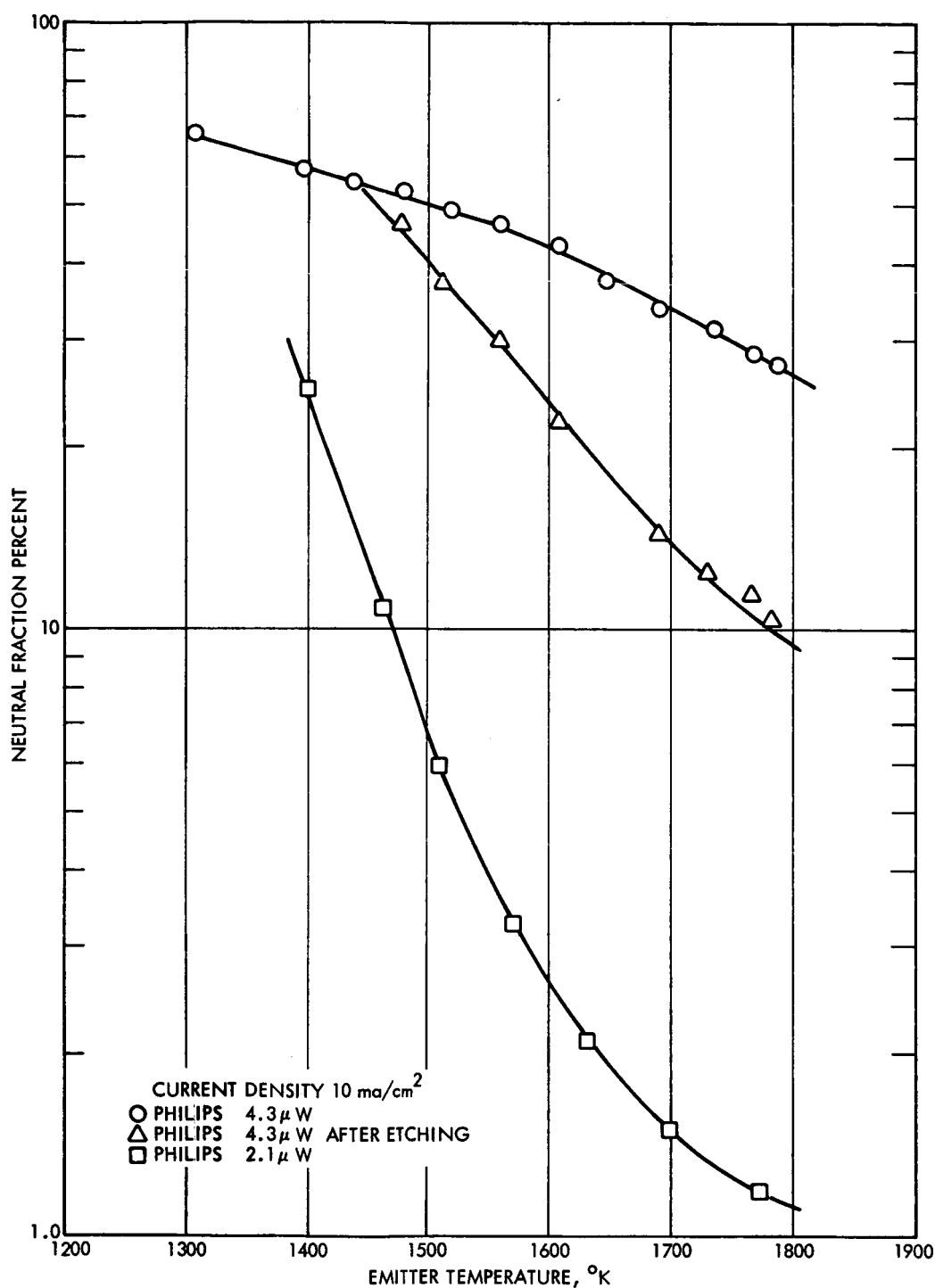


Figure 23. Cesium neutral fraction versus porous tungsten temperature for pellets of different pore size and surface preparation.

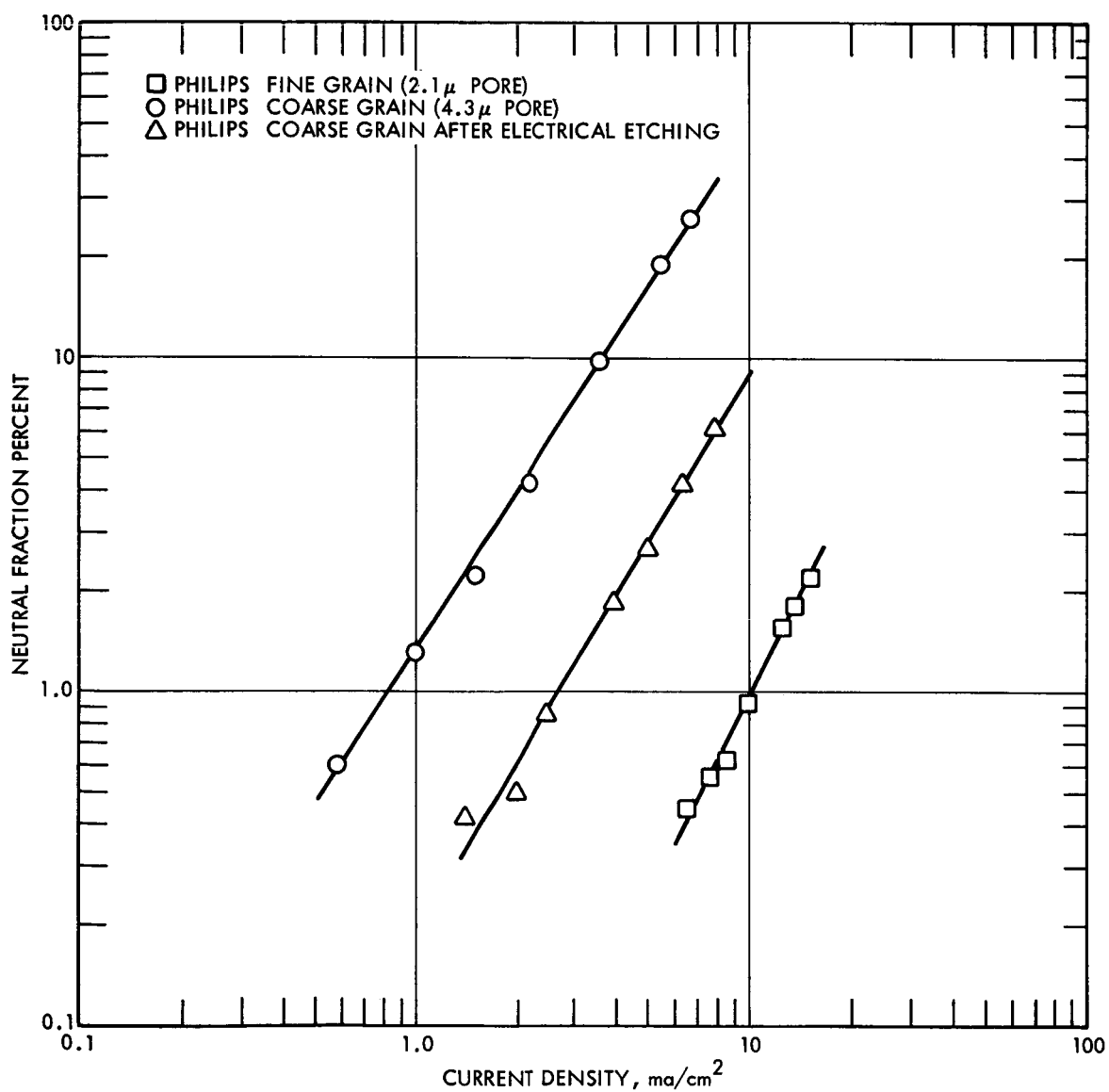


Figure 24. Cesium neutral fraction versus ion current density for the same pellets shown in Fig. 23.

leading to the surface. There exists also, the possibility that some material deposited specifically on the surface, causes more rapid sintering. Also, as mentioned earlier, is the suggestion of Koppius of Semicon of Lexington that oxygen within the porous tungsten can transport tungsten from the interior to the surface via volatilization of WO_3 . Presumably deposition would occur at the surface because of the low surface coverage of oxygen maintained by the vacuum pumps.

Besides merely opening up the surface, the proper etching might produce a better contour of the pore exit. Since it is only the geometry of the surface that affects the ion emitting properties of the porous tungsten, it is felt much more work can be done in this area.

The method of etching employed by us, was at first the simple A.C. electrolytic etching in hydroxide. First we used CSOH in distilled water when it was not possible to follow by complete rinsing.. Later we used D.C. etching in concentrated KOH so as not to redeposit any material on the surface and to keep the tungsten oxide in solution. We followed by boiling in concentrated KOH, followed by thorough rinsing by pressure flow of distilled water and acetone. The permeability checks were made after a mild drying in an air oven.

Microphotographs taken of the surface after operation, but without etching, and after operation with previous etching, reveal

clearly the more open nature of the etched material. This is illustrated in figures 25a and 25b. It is interesting to compare this type of etching with that which is attributed to oxygen. This is shown in figures 26a and 26b. Since this type of etching is accomplished at high temperature, it could well be more stable against change with time.

Results of Measurements on Porous Tungsten made from Graded Spherical Powder

Results on porous tungsten manufactured by Electro-Optical Systems, Inc. of Pasadena, California, are preliminary. One type of material, designated by them as E-6⁽²²⁾ was machined by us from a copper impregnated billet, vacuum distilled to rid it of copper, and rhodium brazed to a molybdenum feed tube. The results shown here were after etching opened the surface since the initial testing indicated a very poor surface pore count. The neutral fraction versus current density at 1850°K is shown in figure 27. The improvement accomplished by etching is clear. Also, the improvement due to operating in oxygen is apparent. The neutral fraction versus emitter temperature is shown in figure 28. The acceptable low neutral fraction to within 50°K of critical temperature is a clear indication of the superior high current density characteristic of this material. The not-too-high temperature minimum and increase at higher temperature are more reminiscent of solid tungsten data.

Electron "Drain Currents"

Electron currents from the negative accelerator electrode

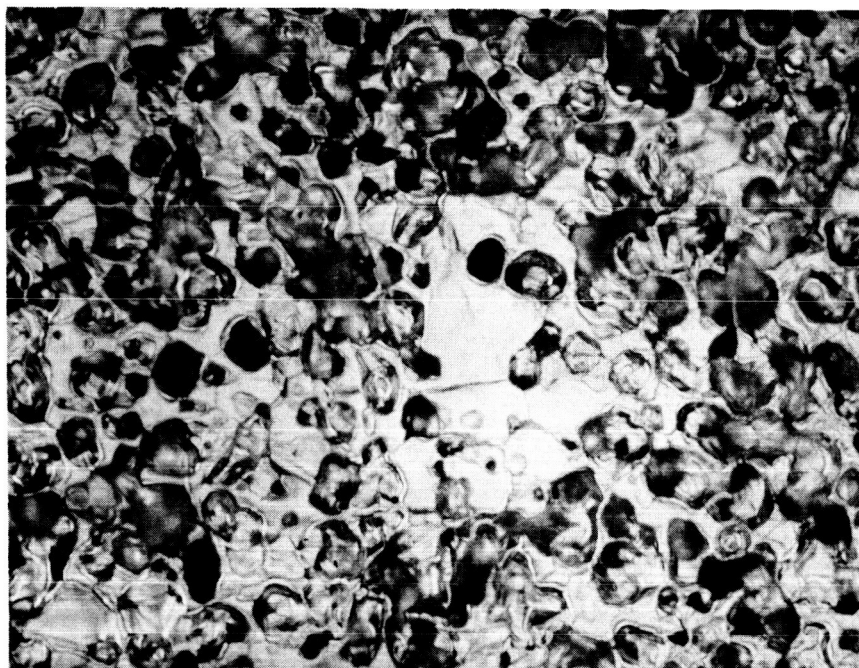


Figure 25a. Microphotograph of the coarse grain ($4.3\ \mu$) porous tungsten surface after electrolytic etching and cesium ion operation (540X)

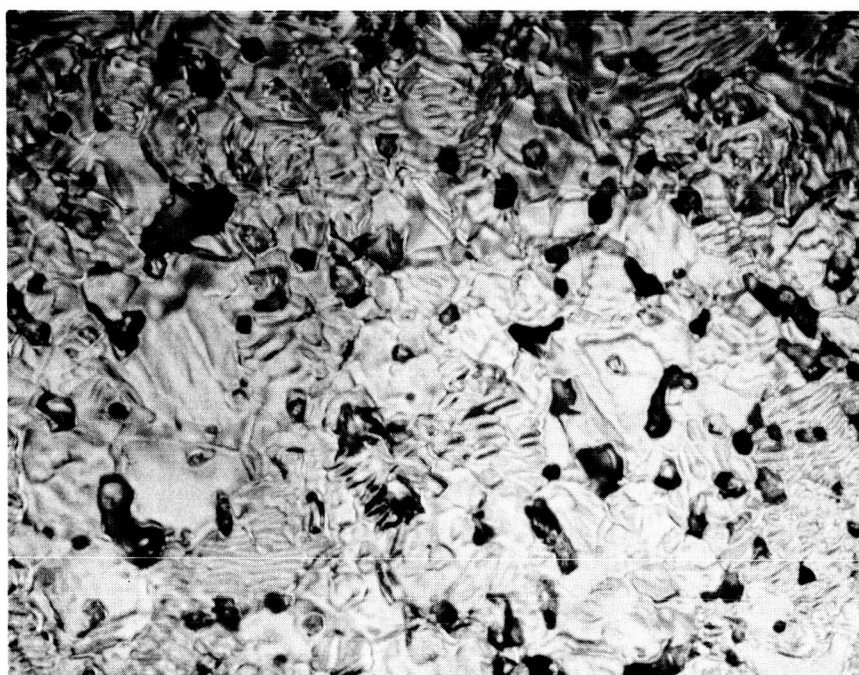


Figure 25b. Microphotograph of a lightly etched section of the same surface shown above, indicating the near solid appearance of the surface before etching (540X).

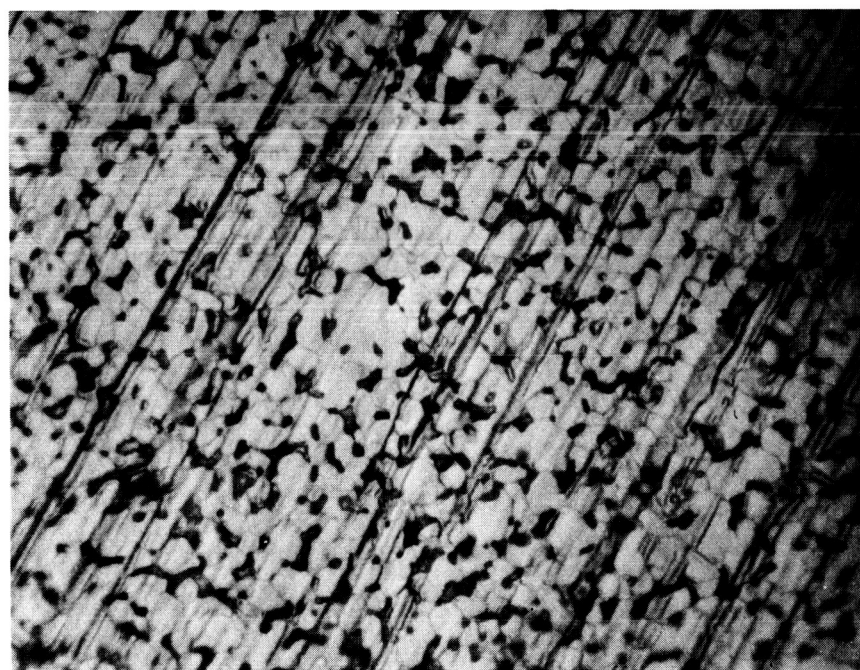
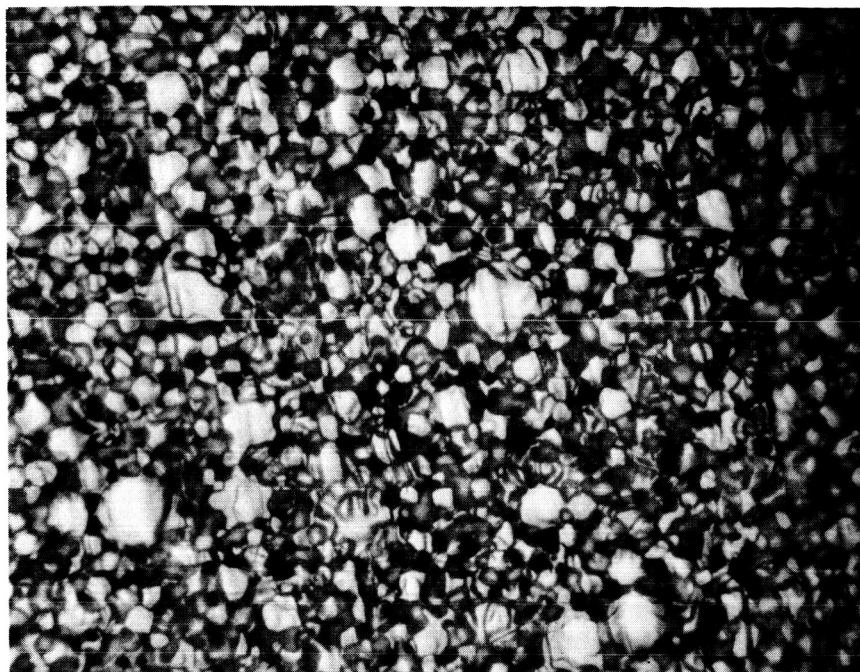


Figure 26. Two sides of porous tungsten pellet after vacuum distillation of copper illustration, etching of one side (540X)

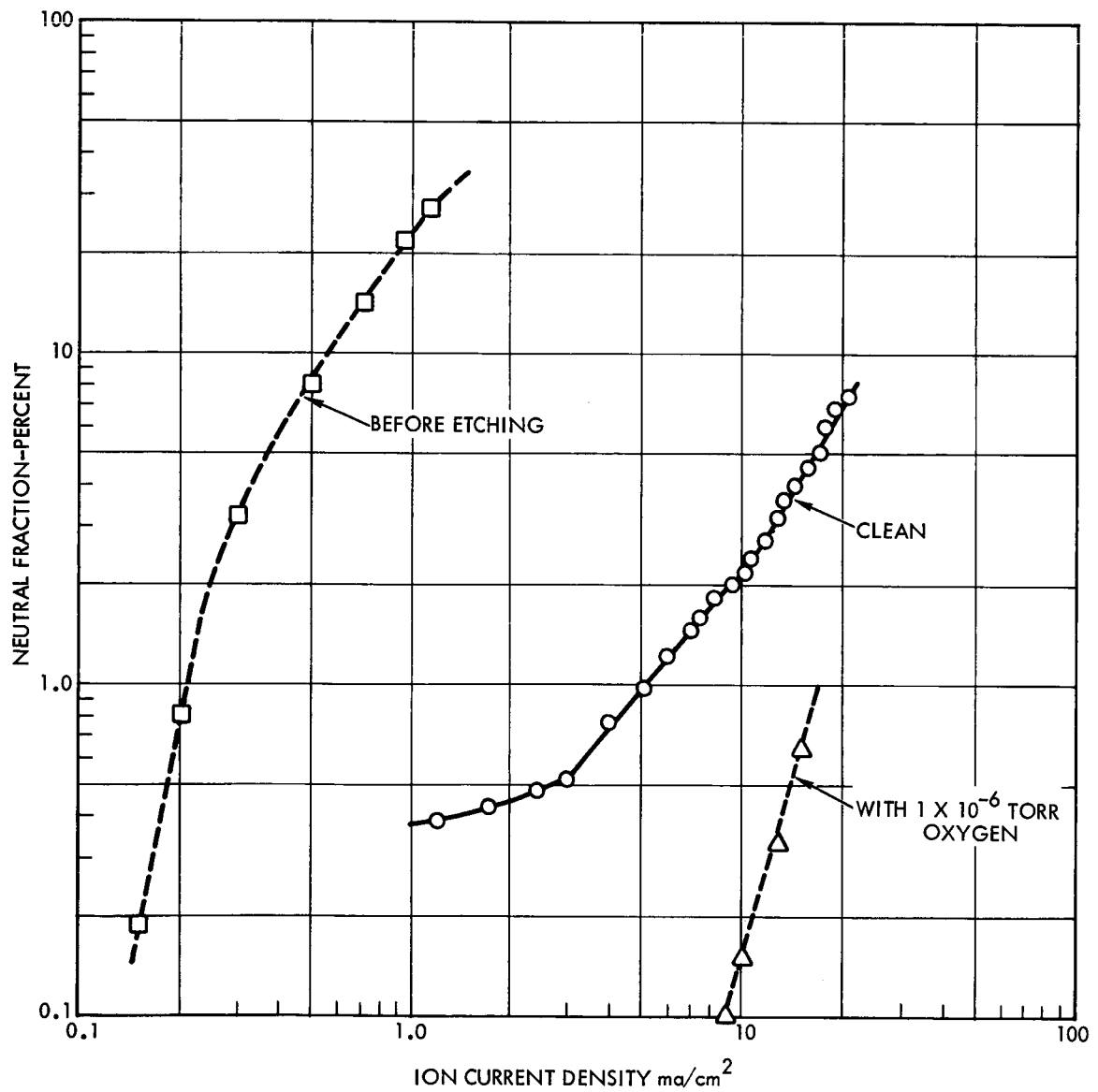


Figure 27. Cesium neutral fraction from E.O.S. Sample E-6 under different conditions at different ion current densities.

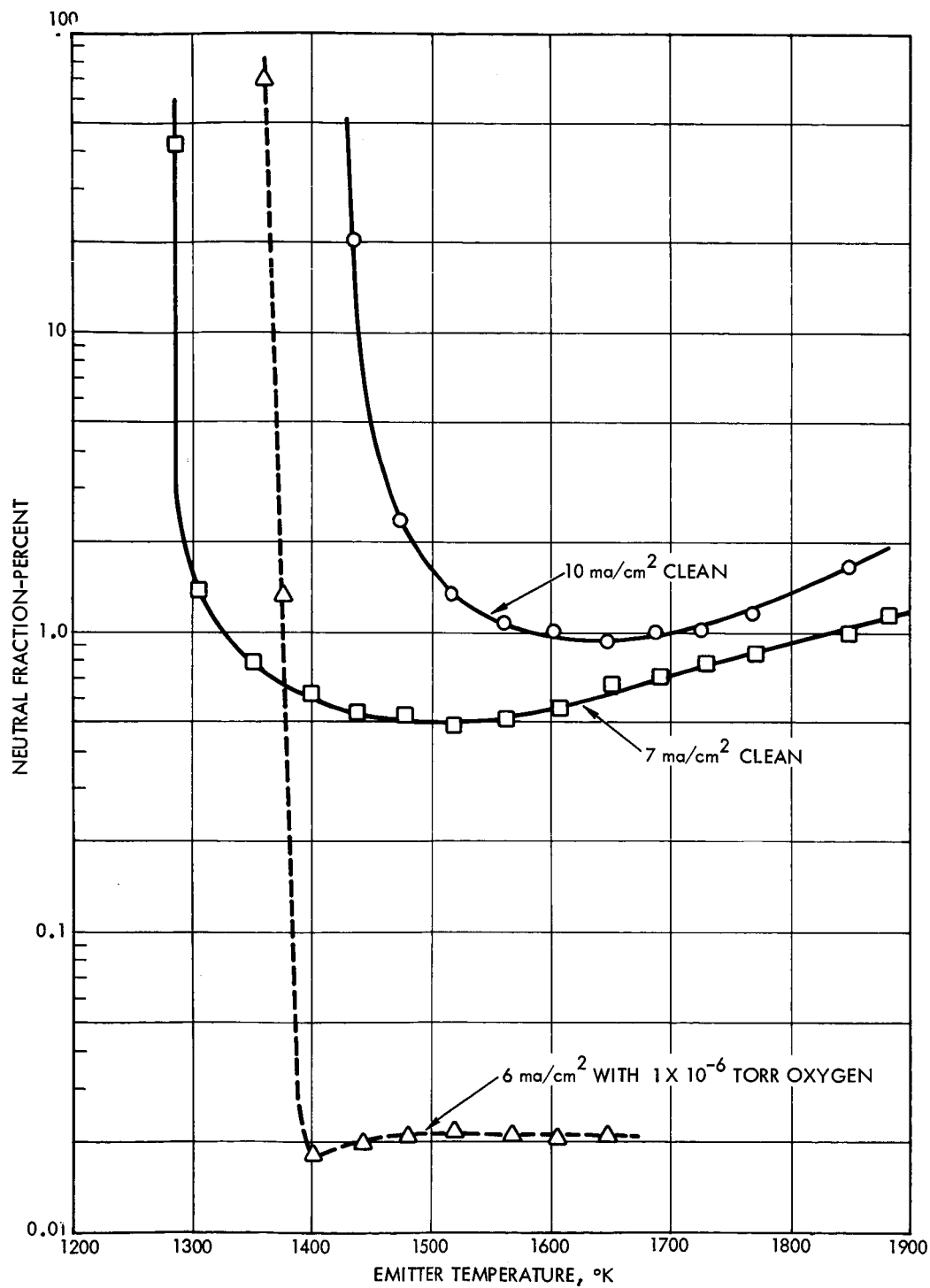


Figure 28. Neutral fraction versus temperature for E.O.S. E-6 material after etching.

to the positive porous tungsten emitter are very troublesome. They can heat the source and prevent temperature control of the emitter. They mask other currents to the accelerator. If some of these currents get to the collector they reduce the ion current reading. They load down high impedance power supplies. In our present system without temperature control of the copper accelerator, they prevent us from achieving high current density operation. These currents require cesium to activate a low work-function surface; and yet they persist for long times after the cesium supply is interrupted. They often are a large part thermionic, requiring radiation from the emitter; and yet they are observed at room temperature and most often decrease at very high temperatures. The currents are very sensitive to electric field and yet drain currents have been so severe that at only a few volts, the normal ion current is exceeded and the engine cannot be turned on.

The observations indicate a combination of thermionic and field emission currents enhanced by the low work-function associated with cesium. Usually admission of 1×10^{-6} torr of oxygen immediately reduces the drain current by more than a thousand. This observation is consistent with our previous conclusion that bulk cesium oxides have inferior electron emission, especially if oxygen rich. If the vacuum is good, the cesium can be reduced to zero and the temperature lowered to room temperature and still the currents will remain at nearly their hot value. These currents

are obviously field emission currents. $\log i/v^2$ is plotted vs. $\frac{1}{v}$ in figure 29. Field emission currents not affected by space charge should plot as straight lines.

These currents are erratic, but usually get worse with time. This is attributed to roughening the surfaces by building up whiskers from evaporated material, or flaking of coatings.

Another type of spurious current has been observed many times. It has always been observed from surfaces below room temperature and has been particularly bothersome in our neutral detectors. It has occurred from copper, nickel, brass, gold, and steel. It is electrons from a negative electrode. It requires a cesium arrival rate and some reasonable electric field to start the current. Once started it does not need a high electric field or much, if any, cesium to sustain it. Once the current is interrupted and the voltage reapplied, the current is absolutely zero. With time, if an electric field and cesium is present, the current starts up again. It starts more rapidly at higher fields. Excess oxygen usually stops the current from starting. Heating the electrode stops the current. No explanation of this current is available.

CONCLUSION

The cesium neutral, ion, and electron emitting characteristics of porous tungsten have been determined when the surface is clean, covered with varying degrees of oxygen, and when carbided. Both oxygenated and carbided tungsten emit fewer neutrals than clean

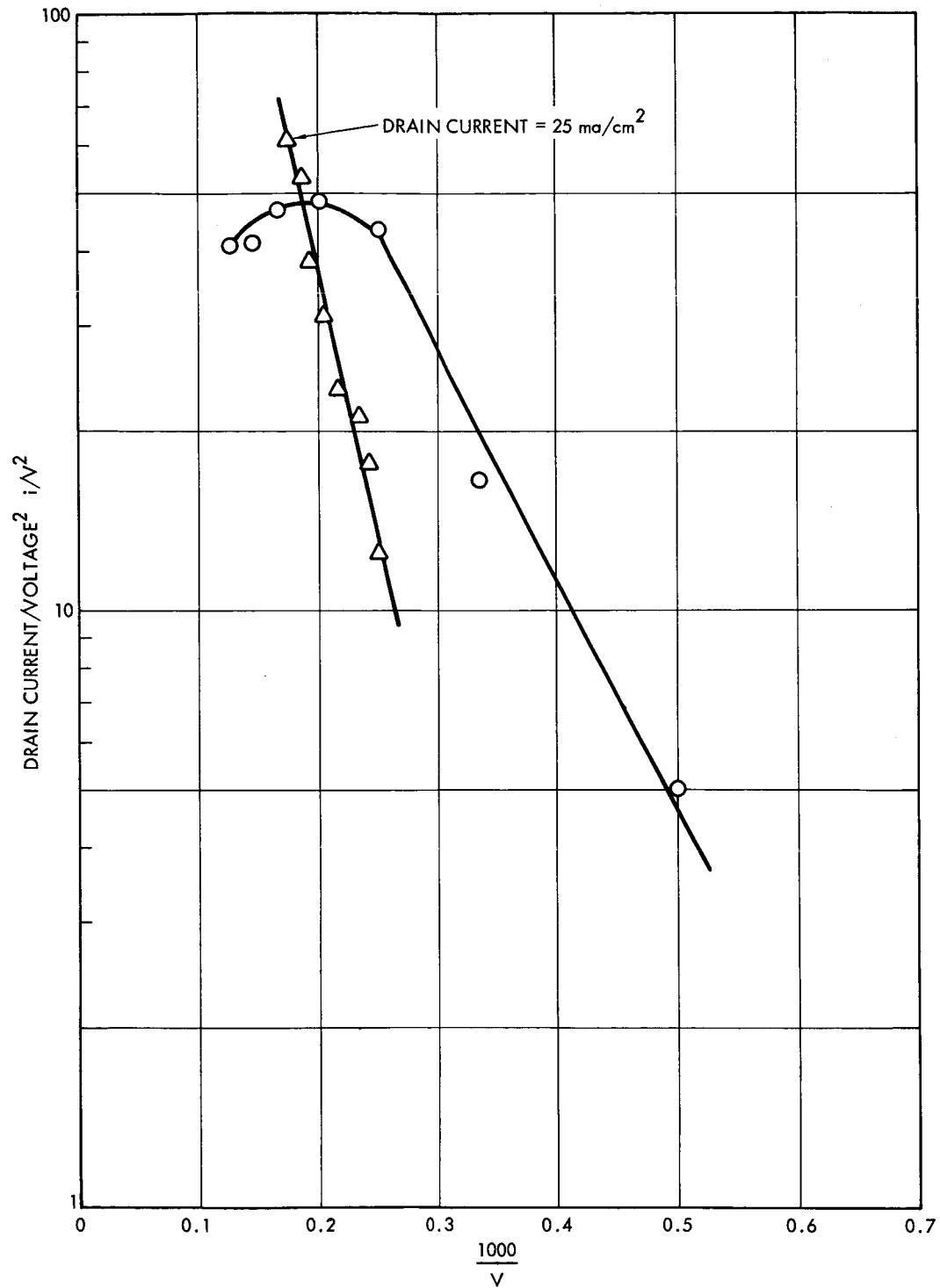


Figure 29. Variation of field emitted drain current with voltage at room temperature with no cesium replenishment.

tungsten. Oxygenated tungsten has a higher carbided tungsten and a lower critical temperature than does clean tungsten. At high ion current densities, if there is insufficient pore density, the neutrals are excessive unless a much higher than critical temperature is used. The occurrence and transport of oxygen, carbon and other impurities have been discussed. Observations and a brief study of spurious electron currents have been listed.

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APPENDIX

**CESIUM NEUTRAL AND ION EMISSION FROM
CARBURIZED AND OXYGENATED POROUS TUNGSTEN**

CESIUM NEUTRAL AND ION EMISSION FROM
CARBURIZED AND OXYGENATED POROUS TUNGSTEN*

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TRW/Space Technology Laboratories

Introduction

In the use of hot porous tungsten to produce cesium ions for electrical propulsion, the degree of tungsten purity is of extreme importance. Materials affect the tungsten performance mainly altering the work-function, the cesium binding energy, and the emissivity. The materials that raise the work-function lower the ratio of neutral emission to ion emission. Materials that lower the work-function increase the neutral emission - often above the ion emission. If the binding energy is increased, the critical temperature necessary to evaporate a given current density of ions will increase. If the binding energy is decreased, the critical temperature will be lower.

Tungsten can be brought to a very high degree of purity simply by raising its temperature, causing foreign materials to diffuse to the surface and evaporate. In the case of practical ion emitters, however, the practical difficulties of heating large areas, the temperature limitations imposed by the brazes, and deleterious effects of further sintering, interfere with the use of this method. The experimenter may, therefore, often be working with other than clean tungsten.

This paper describes experiments on porous tungsten emitters in which special measures were taken to control surface conditions. Ultra high vacuum was maintained, emitters were designed to allow prolonged heating to 2000°K, capability for surface sputtering was provided, and controlled amounts of impurities could be introduced.

Results are presented showing that oxygen decreases neutrals, but increases critical temperature. Carbon decreases neutrals and decreases

*This work supported by contract NAS 3-2524 through Lewis Research Center.

the critical temperature, but raises emissivity. Calcium increases neutrals and increases critical temperature. These observations result from careful repeated study of each of these materials deposited on tungsten which had first been cleaned by high temperature operation in high vacuum followed by sputtering.

Experimental Procedures

The measurements were made on one inch diameter porous tungsten discs manufactured by Semicon of California. The ions are focused and accelerated by two fine grids of tungsten wires. These grids can be heated to 2600°K so as to keep the surface clean. Electron currents from the accelerating grid to the source during ion emission, and from the focusing grid during electron emission are thus eliminated. When maintained hot and at a positive potential, the grids can also be used to sputter the tungsten source since a fraction of the cesium from the source will be intercepted, surface ionized, and accelerated back to the source.

A hot ribbon neutral sensor off to one side of the ion beam "sees" the surface of the porous tungsten through the fine set of grid wires. Although the neutral detector measures propellant utilization as modified by the accelerating structure rather than the desired true neutral fraction, in this case because of the small amount of neutral scattering by the fine grids, the two are essentially the same.

The vacuum obtained by a Welch "turbomolecular" pump is oxygen-free and hydrocarbon-free, as monitored by a mass spectrometer mounted in the system. A large copper surface at liquid nitrogen temperature surrounds the ion source, cools the neutral detector and condenses cesium and water vapor. The total pressure when operating is a few times 10^{-8} torr, and is mostly untrapped cesium.

A clean tungsten surface is obtained by first heating in oxygen to remove carbon, operating for hours at a relatively high ($5\text{--}10\text{ ma/cm}^2$) cesium ion current density at 2000°K , and then sputtering. Such a

surface can then operate clean for many minutes. During this time a leak of oxygen producing a pressure of 1×10^{-8} torr will detectably alter the surface condition. Because the measurements were made on thoroughly cleaned porous tungsten at relatively low ion current density where the pore distribution has little effect, these data are believed to be valid for all clean porous tungsten regardless of manufacturer.

The carbided surface is produced by cracking hydrocarbon vapors (C_2H_2 , CH_4 , C_2F_4 , etc) and stabilizing by high temperature operation. The short exposure time (minutes) and the low pressure (a few times 10^{-6} torr) results in a very thin coating of W_2C a few microns thick. It has been identified by X-rays. This surface can be cleaned up by long (at high T) exposure to oxygen. It is noteworthy that oxygen at any pressure up to 10^{-5} torr or more has no effect on the electronic properties of this surface for considerable periods of exposure. This effect and the clean up of carbon is attributed to the rapid formation and evaporation of CO.

The qualitative features of an oxygenated surface have been gathered over a long period of time on many different samples of porous tungsten. The quantitative effect depends on the degree of oxygenation, cesium ion current density, trace impurities, and the past history of the surface. The carbided surface, on the other hand, exhibits the same quantitative characteristics time and time again on different sources carbided in different manners. This surface is also much less sensitive to traces of poisoning contaminants. The truly clean tungsten surface is harder to achieve and maintain; after the tungsten is essentially clean, the remnant surface contaminants such as oxygen can be sputtered off.

Experimental Results

Clean Tungsten

In Figure 1 is plotted the electron current density from clean porous tungsten fed with cesium. The feed rate was such as to produce

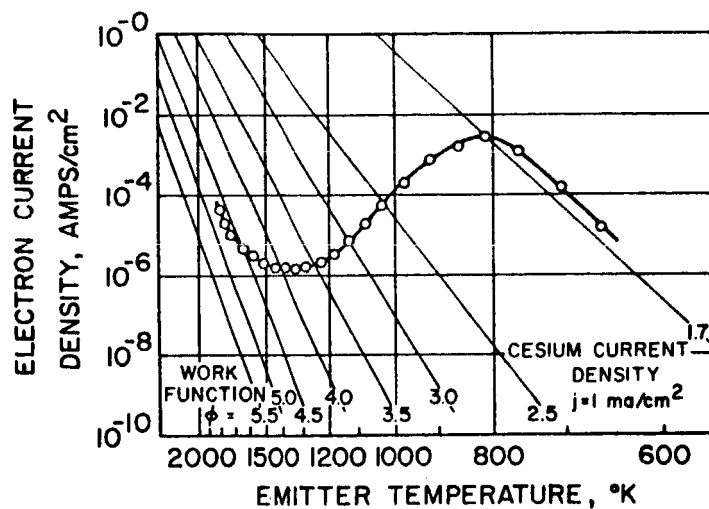


FIGURE 1. ELECTRON EMISSION "S" SHAPED CURVE FOR CLEAN POROUS TUNGSTEN IONIZER

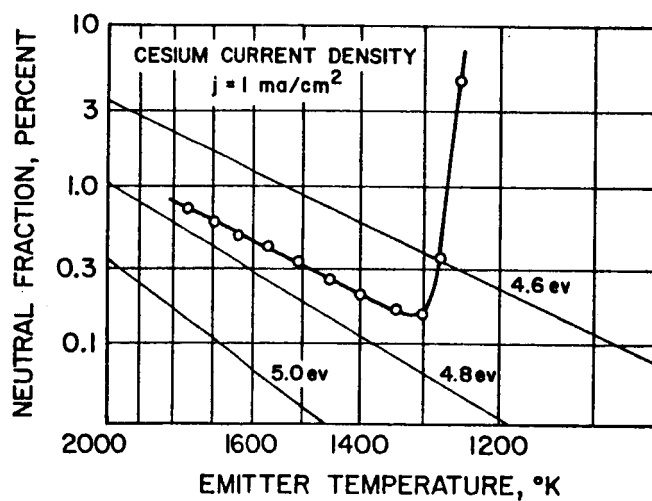


FIGURE 2. CESIUM NEUTRAL FRACTION VERSUS TEMPERATURE FOR CLEAN POROUS TUNGSTEN IONIZER

1 ma/cm² ion current density, if the voltage were reversed. Plotted lightly in the background are constant work-function lines, based on the Richardson equation, $j = 120 T^2 \exp(-e\phi/kT)$ amps/cm². When the experimental points lie parallel to these lines the surface is maintaining a constant work-function. The value of the work-function of any point can be interpolated from its position on the experimental curve relative to the lines of constant ϕ . We can see in this instance that at high temperature, cesium coverage is essentially zero, and we find the work-function of this clean porous tungsten to be 4.7 volts. At lower temperatures, the cesium sticks, lowers the work-function and causes the electron emission to increase. The temperature at which the electron current crosses the 3.7 volt line (1300°K in Figure 1) is approximately the critical temperature for ion emission.

Under different surface conditions the "S" shaped curve may depart from the constant work-function line at higher temperatures and may increase more rapidly to the right. The critical temperature then will be higher. The portion of the curve farther to the right relates to the adherence of large cesium coverages and has no bearing on ion production.

In Figure 2 we see the percentage fraction of neutral cesium emitted from the same surface during ion operation at high voltages. At the right, the temperature is below critical and the neutrals are nearly 100%. The critical temperature is indeed 1300°K. Constant work-function lines are shown, based on the Saha-Langmuir equation, which predicts that the fraction of the total cesium emitted as neutrals will be $\alpha = (1 + \frac{1}{2} \exp. (\phi - V_i)/kT)^{-1}$ where the cesium ionization potential V_i is 3.9 volts. (A report¹ by Teem and co-workers shows that when a patchy surface is involved, it is the electron work-function as we measure it with $A = 120$ that should be used in this equation to predict neutrals.) At high temperatures the cesium coverage is very low and the work-function is that of clean tungsten. The resulting neutral fraction and its temperature dependence agrees reasonably well with the work-function found from the "S" curve.

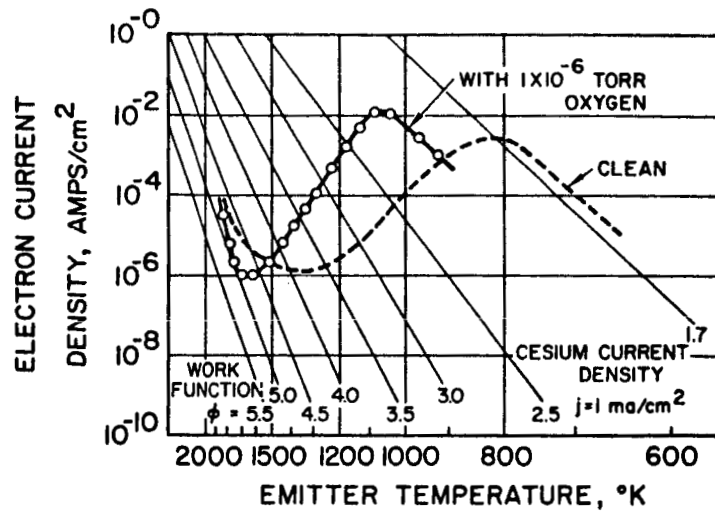


FIGURE 3. ELECTRON EMISSION "S" SHAPED CURVE FOR OXYGENATED POROUS TUNGSTEN IONIZER

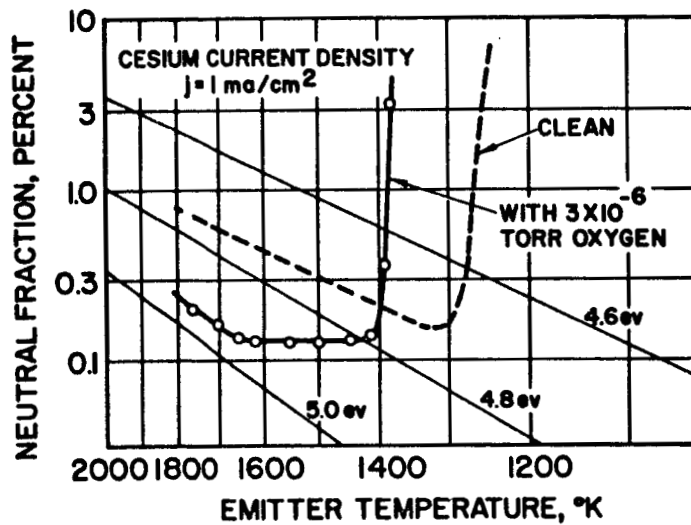


FIGURE 4. CESIUM NEUTRAL FRACTION VERSUS TEMPERATURE FOR OXYGENATED POROUS TUNGSTEN IONIZER.

Oxygenated Tungsten

Figure 3 shows the "S" shaped curve for oxygenated tungsten. The dotted curve for clean tungsten is included for comparison. For the higher temperatures to the left, we see a high work-function decreasing towards the value for clean tungsten. The abrupt steep rise as the temperature is decreased indicates that the cesium has a high binding energy and that a high critical temperature will result. Although oxygenated tungsten in vacuum results in a larger low temperature maximum, the continuous maintenance of an oxygen pressure in this case suppresses the electron emission at low temperature. In Figure 4 we see that the critical temperature is increased and that the neutrals are lower, relative to clean tungsten. The broad flat minimum region indicates the adherence of a sizable cesium coverage to quite high temperatures, again indicating a high binding energy.

Carburized Tungsten

In Figure 5 the "S" shaped curve for carbided tungsten is shown. The work-function is 4.9 volts. Also as evidenced by the low valley, the binding energy is lowered, predicting a lower critical temperature (1210°K). It is of interest to note that the binding energy for large cesium coverages is increased, giving a larger low temperature peak emission. This characteristic is in close analogy to the effect of W_2C on electron emission from barium impregnated porous tungsten. At high temperatures ($T > 1000^{\circ}\text{K}$) W_2C is used to suppress electron emission by allowing the barium to evaporate. At low temperatures, electron emission is enhanced from W_2C areas².

Figure 6 shows the neutral fraction versus temperature for carbided tungsten. We see that the critical temperature is lower, that the neutrals are lower, and that the strong temperature dependence as governed by the Saha-Langmuir equation is evidenced.

The improved ion emitter properties of carbided tungsten is offset by its higher thermal emissivity, which is approximately 0.4.

Calcium, Fluorine, and Other Contaminants

Calcium was studied and found to be a bad poison - it appeared

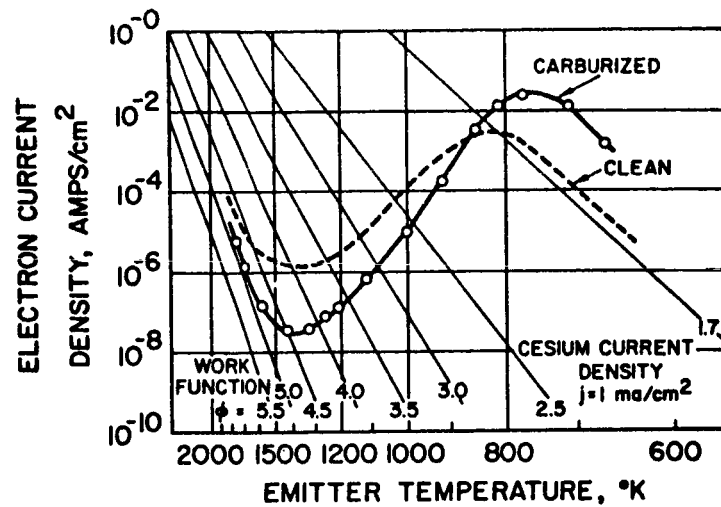


FIGURE 5. ELECTRON EMISSION "S" SHAPED CURVE FOR CARBURIZED POROUS TUNGSTEN IONIZER

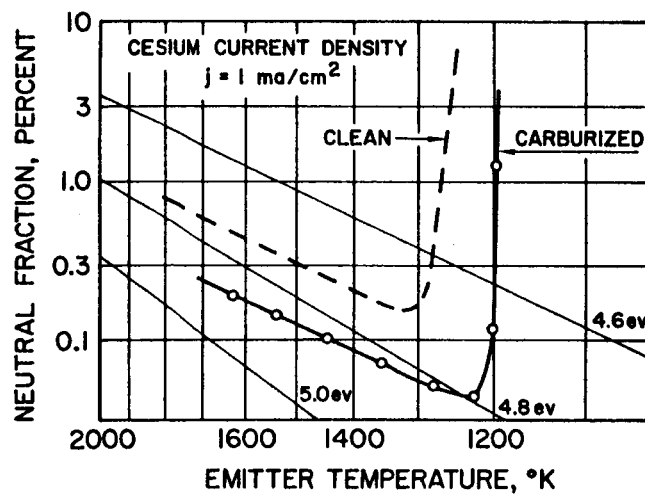


FIGURE 6. CESIUM NEUTRAL FRACTION VERSUS TEMPERATURE FOR CARBURIZED POROUS TUNGSTEN IONIZER

both to lower the work-function, thereby producing high neutral emission, and also to hold the cesium tightly, producing a high critical temperature. High temperature operation was necessary to lower the calcium concentration on the surface by evaporation. A high pseudo-critical temperature existed where the diffusion rate to the surface matched the evaporation. This temperature was often above 1700°K.

Fluorine acts like oxygen. It raises the critical temperature and lowers the neutrals. Silicon and boron were found to have little effect on ion and neutral emission, although they raised the tungsten work-function slightly.

The presented data have all been at the relatively low current density of 1 ma/cm² in order to graphically illustrate the basic effect of work-function and binding energy. The increase of neutrals with current density because of insufficiently fine pore distribution is barely seen here. As pointed out by the work of Hussman³ the neutrals increase at higher ion current densities - badly so with a coarse grain porous tungsten and less so with a fine grain porous tungsten. Also the critical temperature is less well defined at high ion current densities with a large range of temperatures where an increase in temperature decreases the neutrals. High current densities up to 16 ma/cm² on many different porous tungsten samples have been studied by the authors, and the different characteristics of high current density ion emission and the data presented here are not contradictory and are due to the pore distribution.

Conclusion

An oxygenated tungsten surface is identifiable from its "S" shaped curve by its high bare work-function and high cesium coverage at ion operating temperatures and from its ion emission by the high critical temperature and the small constant percentage value of neutrals at higher temperatures. A carbided surface is identifiable from its "S" shaped curve by its stable 4.9 volt work-function insensitive to oxygen and the deep minimum, and from its ion emission by the low critical temperature and the rapid rise of

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